A study of matter-antimatter compounds: spontaneous rearrangement in anti-hydride molecules

博士論文

A study of matter-antimatter compounds: spontaneous rearrangement in anti-hydride molecules

（物質・反物質化合物の研究：反水素化分子における自発転位）

山下琢磨

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Thesis

A study of matter-antimatter compounds: spontaneous rearrangement in anti-hydride molecules

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This document is a brief summary of the present thesis.

Chapter 1 Introduction

An atom is the minimum unit of matter in chemistry. Atom-antiatom reactions can be the first step of matter-antimatter study. This thesis describes theoretical studies on matter-antimatter compounds represented by "anti-hydride" molecules. As one of the universal aspects in matter-antimatter compounds, a perspective of "spontaneous rearrangement" inside a single molecule driven by particle-antiparticle attraction is proposed. Understanding of the spontaneous rearrangement in anti-hydride molecules will be a foundation for matter-antimatter chemistry.

Recent techniques for generating, cooling, manipulating and detecting antiparticles allow us to synthesize antimatter consisting of positrons and antinuclei for not only strict test of fundamental physics but also new chemistry between matter and antimatter. If a part of matter is replaced with antimatter the electric balance in the matter would drastically change because the signs of the charges of the containing particles in antimatter are opposite to those in matter. Interactions between matter and antimatter provides exotic chemical properties of compounds, a variety of reactions and enhancement of hidden quantum effects in matter. A matter-antimatter compound will be a touchstone of the universality and diversity of chemistry and it provides challenging theoretical/experimental problems. Since the admixture of matter and antimatter involves phenomena such as nuclear acceleration, neutralization of leptonic cloud and auto-dissociation of compounds with large energy transfer, that cannot be treated in a conventional framework of chemistry, prediction and investigation of the matter-antimatter compounds requires a rigid theoretical evaluation of the governing equation which chemistry has based on. Experiments on the matter-antimatter compounds require sophisticated techniques to handle a trace amount of antimatter and measure signals of the compounds. Precise theoretical studies, therefore, highly correlates with the experiments to open matter-antimatter chemistry.

An antihydrogen atom consisting of a positron and an antiproton is the simplest antimatter. Aiming at a test of fundamental physics on matter-antimatter symmetry, a cold antihydrogen source has been developed in these decades. The cold antihydrogen atom may form a compound with an atom: anti-hydride molecule. The anti-hydride molecule is a miniature of the matter-antimatter compounds where correlations among electron, positron, nucleus and antinucleus (antiproton) are involved. For a comprehensive understanding of matter-antimatter compounds and for facilitation of future studies on matter-antimatter compounds as an extension of traditional chemistry, the present thesis proposes a perspective of "spontaneous rearrangement" which usually expresses a molecular structure change driven by automatic transfer of atom(s) on the molecule. In ordinary molecules, since the speed of the nuclear motion is slower than that of electrons, the structure of the molecule can be associated with the nuclear positions. A plurality of nuclei share electrons in the molecule and the electronic state can be written in molecular orbitals (MO). The molecule clearly consists of atoms and the molecular orbitals can be well approximated by a linear combination of atomic orbitals (LCAO). In the matter-antimatter compound, on the other hand,

the atom as a constituent of molecule is no longer unique. While the electron and nucleus can form an atomic fragment and the positron and antinucleus can form antiatomic fragment, the electron can also form positronium-like fragment with the positron and the nucleus can form a quasi-atomic fragment with the antinucleus. Since the attractive interaction between the nucleus and antinucleus accelerates the velocity of nuclear motion, the "structure" of the matter-antimatter compound cannot be simply associated with the (anti)nuclear positions. The electrons are not shared by the antinuclei and the positrons are not shared by the nuclei, which means the ordinary ideas of molecular orbital cannot be adopted naively to the matter-antimatter compounds. In other words, the locality of nuclei that the ordinary molecules have is violated in the matter-antimatter compounds and the association between electrons and nuclei is disturbed by the positrons and antinuclei. The structure of matter-antimatter compound may be understood from a viewpoint of the various associations co-existing in the compound.

Generally the matter-antimatter compound is not stable against auto-dissociation via rearrangement because the de-excitation of the quasi-atomic state of nucleus and antinucleus can eventually deposit enough energy to the light particles (electrons/positrons) for dissociation. Such a large energy transfer to light particles can be seen in matter systems as the Auger electron emission; however, the matter-antimatter system has additional degrees of freedom of positronium. The auto-dissociation process of the matter-antimatter compound may be interpreted as an intramolecular reaction from a point of view that the nuclear/antinuclear positions drastically changes together with electronic/positronic states. It is characteristic for the matter-antimatter compound that such intramolecular reaction occurs even in a small system.

The perspective of microscopic spontaneous rearrangement driven by particle-antiparticle associations would help us to understand both of the structure and intramolecular reactivity of the matter-antimatter compounds systematically. The main purpose of this thesis is to investigate how the spontaneous rearrangement contributes to the energy, structure and stability of anti-hydride molecules and its sub/related systems.

Overview of this thesis

The present thesis is constructed from studies on positronic atoms, hydrogen anti-hydride molecule, and positronium anti-hydride molecule. Chapter 2 describes general theoretical aspects of the nature of bound and resonance states and also of framework of calculations. Chapter 3 explains studies on positronic atoms. In particular, an investigation on loosely bound states of positronic alkali atoms and resonance states caused by ion-dipole interaction are focused. Chapter 4 describes resonant molecular states of hydrogen anti-hydride molecule and its subsystem, antiprotonic hydrogen atom. The stability and structures are investigated by a fully quantum mechanical treatment. Chapter 5 studies a bound state of positronium anti-hydride molecule, especially on the structure having both of molecular and atomic features. A reaction between the positronium and antihydrogen atom which has been expected to open a new source of antimatter is also investigated. Chapter 6 summarizes the discussion on the spontaneous rearrangement of anti-hydride molecules and remarks about outlook.

Chapter 2 Theory

Basic theoretical aspects behind the present thesis are described in this chapter. Some of them are briefly summarized here. Atomic units (a.u.; $m_e = \hbar = e = 1$) are used throughout this paper, except where mentioned otherwise.

Bound, resonance and scattering states

States of atom/molecule can be classified into bound, scattering and resonance states. The bound state is stable against auto-dissociation and the scattering state is a state where the constituents are dissociated. The resonance state is a quasi-bound state which dissociates in a certain lifetime. As an example, we consider a compound of atoms A and B. A bound state is located below the lowest dissociation threshold A + B. The energy spectrum of the bound states are discretized as shown in Fig. 1 (a). As shown in Fig. 1 (b), when the interaction between A and B has a potential barrier, there can be a resonance state called a shape resonance state above the lowest dissociation threshold. The shape resonance state is a quasi-bound state which dissociates into A + B having a certain lifetime via quantum tunneling effect. There could be another type of resonance state called Feshbach resonance state. The Feshbach resonance state is, for example, a quasi bound state of an excited atom A^* and B. As shown in Fig. 1 (c), the Feshbach resonance state of A^* and B is located in the potential between them and it can dissociate into A + B. When the interaction between A^* and B has a potential barrier, a resonance state having both aspects of the shape and Feshbach resonance states could be possible. Such resonance state has two ways of dissociation into A + B or A^* + B.

Variational principle

We consider a Schrödinger equation for a given quantum few-body system,

$$H\psi_n = E_n\psi_n, \tag{1}$$

where E_n is the n-th eigenvalue and ψ_n is the corresponding eigenfunction. We assume $E_0 < E_1 \leq \cdots$ and $\{\psi_0, \psi_1, \cdots\}$ is a complete orthonormal system. The lowest eigenstate is assumed to be a bound state having a discrete energy. For a given wavefunction ϕ which can be expanded by $\{\psi_0, \psi_1, \cdots\}$ as

$$\phi = c_0\psi_0 + \sum_{i\neq 0} c_i\psi_i, \tag{2}$$

where $|c_0|^2 + \sum_{i\neq 0} |c_i|^2 = 1$, expectation value of H is

$$\begin{aligned}\langle\phi|H|\phi\rangle &= |c_0|^2 E_0 + \sum_{i\neq 0} |c_i|^2 E_i \\ &= E_0 + \sum_{i\neq 0} |c_i|^2 (E_i - E_0) \geq E_0.\end{aligned} \tag{3}$$

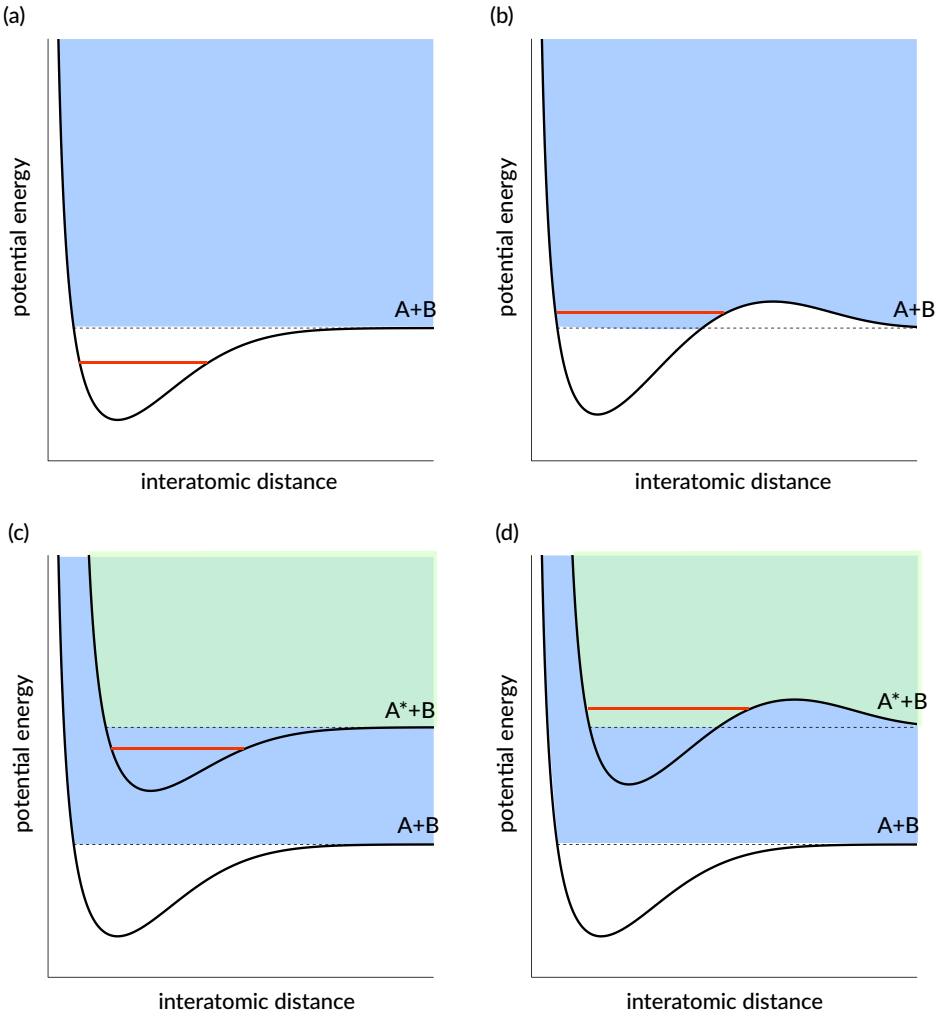

Figure 1: Energy levels of a system consisting of atoms A and B are illustrated for some inter-nuclear potential curves. (a) A case where the potential (black line) has no barrier and the system AB has a bound state (red line) is illustrated. The blue shade is scattering states of A + B which can have continuous energy spectrum. (b) A case where the potential has a potential barrier and the system AB has a shape resonance state (red line) is illustrated. (c) A case where an excited atom A^* and a ground state atom B have a Feshbach resonance state (red line) is illustrated. The higher black line is an inter-nuclear potential associated with a dissociation threshold A^* + B. The green shade is a continuous energy spectrum of scattering states A^* + B. (d) A case where the inter-nuclear potential associated with a dissociation threshold A^* + B has a barrier and a resonance state (red line) has both of shape and Feshbach resonance aspects.

Therefore, the expectation value of H calculated by ϕ gives the upper limit of the exact eigenenergy E_0. This is called the variational principle. If the second eigenenergy E_1 is also discrete, one can find that

$$\langle (H - E_0)\phi | (H - E_1)\phi \rangle = \sum_{i \neq 0,1} |c_i|^2 (E_i - E_0)(E_i - E_1) \geq 0. \tag{4}$$

Then we have

$$E_0 \geq \langle \phi | H | \phi \rangle - \frac{\langle H\phi | H\phi \rangle - \langle \phi | H | \phi \rangle^2}{E_1 - \langle \phi | H | \phi \rangle}, \tag{5}$$

which gives the lower limit of the exact eigenenergy E_0. When the second eigenvalue E_1 is also discrete and we already have the exact eigenfunction ψ_0, adopting a condition $\langle \psi_0 | \phi \rangle = 0$, we have

$$\langle \phi | H | \phi \rangle \geq E_1. \tag{6}$$

The Rayleigh-Ritz variational method utilizes Eq. (3) and evaluates the energy as a function of trial function which has a certain number of variational parameters. A set of parameters minimize the energy gives the upper limit of the exact energy. From Eq. (3), the deviation of expectation value and the exact energy is given in the second order of c_i. In other words, the variational principle is less accurate for the wavefunction itself than the energy. If we construct a trial function Φ by linear combination of finite number (N) of linear independent, square (L_2) integrable functions φ_i, namely,

$$\Phi = \sum_i^N c_i \varphi_i, \tag{7}$$

the eigenenergy as a functional of Φ can expressed as

$$E[\Phi] = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | 1 | \Phi \rangle} = \frac{\sum_i^N \sum_j^N c_i^* c_j H_{ij}}{\sum_i^N \sum_j^N c_i^* c_j S_{ij}}, \tag{8}$$

where $H_{ij} = \langle \phi_i | H | \phi_j \rangle$ and $S_{ij} = \langle \phi_i | 1 | \phi_j \rangle$. A condition that minimizes $E[\Phi]$ respect to c_i^* or c_j ($\partial E / \partial c_i^* = 0$ or $\partial E / \partial c_j = 0$) on Eq. (8) results in a N linear and homogeneous equations,

$$\sum_j^N c_j \left(H_{ij} - E S_{ij} \right) = 0, \tag{9}$$

or in matrix-vector form,

$$\mathbf{Hc} = E\mathbf{Sc}, \tag{10}$$

where $\mathbf{H}$ and $\mathbf{S}$ are N-by-N matrices consisting of H_{ij} and S_{ij}, respectively. The equation (10) is a generalized eigenvalue problem. Obviously, Eq. (10) gives N eigenvalues E_υ ($\upsilon = 1, 2, \cdots, N$). Increasing the number of φ_i in Eq. (7) we get more E_υ which will give upper limits for the exact N eigenvalues. This property is stated in the Hylleraas-Undheim-MacDonald theorem [1, 2].

Complex coordinate rotation method

Resonance energy and width that characterize the feature of resonance state can be treated on complex momentum/energy planes. We consider a resonance state consisting of atoms A and B which has a dissociation state A + B below its energy. On the complex mometum plane, at a pole of S-matrix located at $k = k_{\rm r} - ik_{\rm i}$ ($k_{\rm r} > 0$ and $k_{\rm i} > 0$), the asymptotic form of wavefunction for relative motion of A and B, $u_l(k, r)$, can be written in

$$u_l(k, r) \underset{r\to\infty}{\longrightarrow} A\exp(i|k|re^{-i\beta}) = A\exp\left(i|k|r\cos\beta + |k|r\sin\beta\right), \tag{11}$$

where $k = |k|e^{-i\beta}$. One can see that the wavefunction of resonance state diverges at large distance due to $\exp\left(|k|r\sin\beta\right)$ ($\sin\beta > 0$).

The divergent nature of asymptotic form of the resonance wavefunction can cause difficulty in numerical calculation because the wavefunction cannot be expressed by linear combination of L_2 integrable functions. A complex coordinate rotation (CCR) method (or complex scaling method, CSM) is helpful to avoid the difficulty and calculate resonance energy and width by L_2 integrable functions.

In CCR one scales a radial coordinate r by complex value,

$$r \to re^{i\theta}, \tag{12}$$

where θ is a real number. We define the following transformation operator $\mathcal{U}(\theta)$,

$$\mathcal{U}(\theta)f(r) = f(re^{i\theta}). \tag{13}$$

Here, $\mathcal{U}^{-1}(\theta)\mathcal{U}(\theta) = \mathcal{I}$ ($\mathcal{I}$ is operator of unity). The Schrödinger equation is transformed by $\mathcal{U}(\theta)$ as

$$\mathcal{U}(\theta)H\mathcal{U}^{-1}(\theta)\,\mathcal{U}(\theta)\Psi = E\,\mathcal{U}(\theta)\Psi \tag{14}$$

or

$$H^\theta\Psi^\theta = E^\theta\Psi^\theta, \tag{15}$$

where $H^\theta = \mathcal{U}(\theta)H\mathcal{U}^{-1}(\theta)$ and $\Psi^\theta = \mathcal{U}(\theta)\Psi$. It is noted that $\mathcal{U}(\theta)$ acts on all coordinates of Ψ, namely, $\mathcal{U}(\theta)\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = e^{N\theta/2}\Psi(\mathbf{r}_1e^{i\theta}, \cdots, \mathbf{r}_Ne^{i\theta})$. The foundation of CCR is given by Aguilar, Combes and Balslev [3, 4], and by Simon [5]. The energy spectrum of H^θ is summarized in the following three points:

- The energies of the bound states do not change under the scaling operation ($E = E^\theta$).
- The energies of the scattering states are obtained along with the cuts which rotates clockwise by 2θ angle.
- The poles of resonance states are exposed by the rotated cuts. Since the resonance wavefunctions becomes bound state-like functions, the resonance energies and widths can be determined by L_2 integrable basis functions.

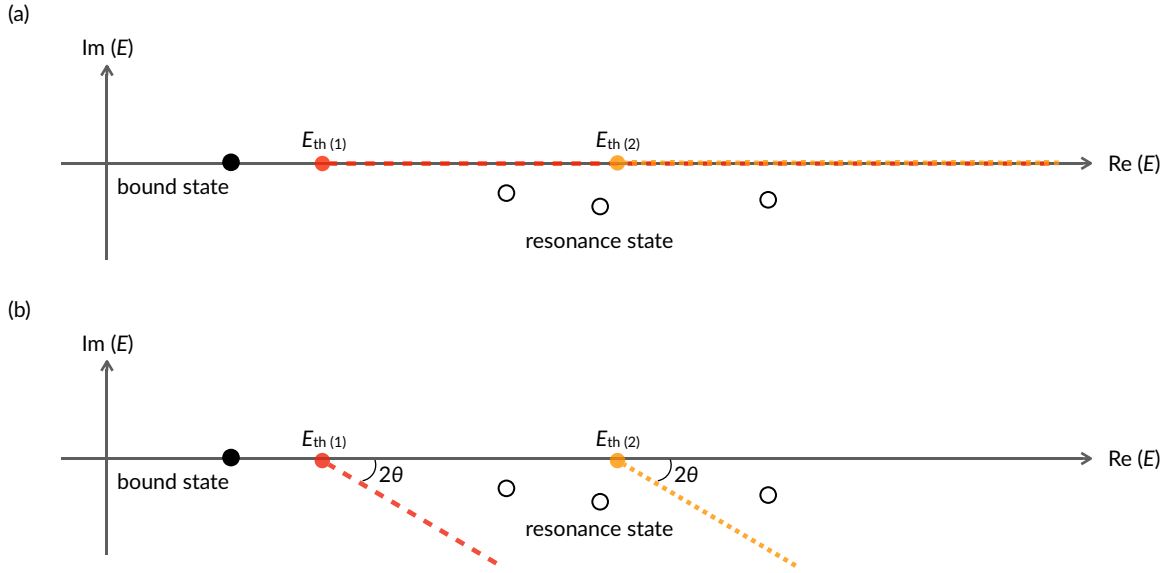

Figure 2: (a) An unrotated energy spectrum of a Hamiltonian H. A bound state is located on the real energy axis below the lowest threshold energy $E_{\mathrm{th}(1)}$. Cuts are on the real energy axis starting from each of the threshold energies and last positive infinite. Resonance states on the second sheet are hidden. (b) A rotated energy spectrum of a Hamiltonian H^{θ}. A bound state does not change its position. Cuts are rotated downwards by 2θ and the resonance states are exposed.

In order to see the third point, we adopt the complex scaling on the Eq. (11),

$$\begin{aligned}\mathcal{U}(\theta)u_l(k,r) = u_l(k,re^{i\theta}) &\underset{r\to\infty}{\longrightarrow} A\exp(i|k|re^{-i(\beta-\theta)}) \\ &= A\exp\left(i|k|r\cos(\beta-\theta)+|k|r\sin(\beta-\theta)\right). \end{aligned} \tag{16}$$

Thus, within $-\pi/2 < \beta-\theta < 0$, $u_l(k,re^{i\theta})$ becomes asymptotically convergent.

The transformation of the energy spectrum is illustrated in Fig. 2. The energy spectrum of H in Fig. 2 (a) shows a bound state pole on the real energy axis below the lowest dissociation threshold energy $E_{\mathrm{th}(1)}$, and some resonance poles located below the real energy axis on the second sheet. The second dissociation threshold energy is noted as $E_{\mathrm{th}(2)}$. Branch cuts runs from $E_{\mathrm{th}(1)}$ and $E_{\mathrm{th}(2)}$ to positive infinity, respectively. When we adopt the complex scaling by $\mathcal{U}(\theta)$, the energy spectrum changes to Fig. 2 (b). The branch cuts rotates clockwise, but the poles does not change. Resonance poles on the second sheet in Fig. 2 (a) are exposed onto the first sheet.

Gaussian expansion method

The present thesis treats both of bound and resonance states of anti-hydride molecules and their sub/similar systems. A precise calculation of such systems requires the evaluation of inter-particle correlations including spontaneous rearrangement. The stability of resonance states can be affected by description of dissociation channels even if the resonance state has different structure from the dissociation fragments.

A Gaussian expansion method (GEM) [6] has been developed to precisely solve the Schrödinger equation of general quantum mechanical few-body systems. GEM performs diagonalization of a Hamiltonian using Gaussian basis functions and provides not only the lowest but also excited eigenstates. A linear combination of Gaussian basis functions written in different coordinate systems facilitates the description of inter-particle correlations and provides a large subspace of the total Hilbert space. The basis functions can be defined in all possible coordinate systems suitable to describe the scattering states. This aspect is another advantage of GEM for the evaluation of resonance states where dissociation states affects their lifetimes. Although energy spectrum of scattering states is discretized due to the finite size of the basis functions, the eigenfunctions of the discretized continuum states reflects a few-body correlation around the eigenenergy and can be used to facilitates the scattering calculation.

GEM has been applied to a variety of few-body systems, such as muonic molecules [7, 8], antiprotonic helium [9–12], cold atoms [13, 14], nucleon systems [15–17] and quark systems [18]. Here the framework of GEM is briefly described.

Here we consider a system consisting of three particles X_1, X_2 and X_3 interacting each other via central forces. The Hamiltonian of this system is written as

$$H_3 = K_1 + K_2 + K_3 - K_{\rm CM} + V_{12} + V_{23} + V_{31}, \tag{17}$$

where K_i is a kinetic operator of particle X_i, $K_{\rm CM}$ a kinetic operator of the center of mass of the system, and V_{ij} is an interaction potential between X_i and X_j.

We introduce three Jacobian coordinate systems $c = 1, 2, 3$ shown in Fig. 3. While the selection of the coordinate system is arbitrary, the Jacobian coordinate systems are suitable to express boundary

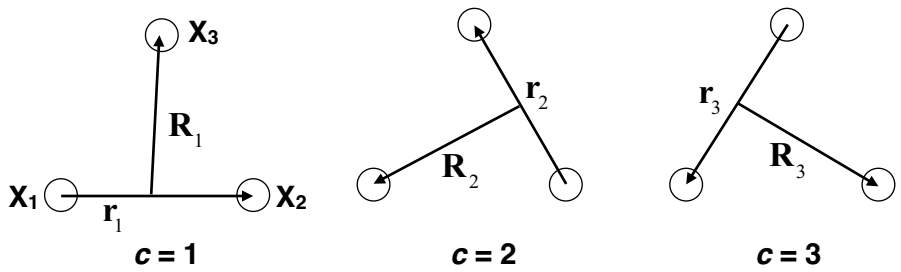

Figure 3: Jacobian coordinate systems for a 3-body system consisting of X_1, X_2 and X_3.

conditions of scattering states. The kinetic operators are written in these Jacobian coordinate systems as

$$\begin{aligned} K_1 + K_2 + K_3 - K_{\rm CM} &= -\frac{1}{2\mu_{12}}\nabla^2_{r_1} - \frac{1}{2\mu_{12,3}}\nabla^2_{R_1} \\ &= -\frac{1}{2\mu_{23}}\nabla^2_{r_2} - \frac{1}{2\mu_{23,1}}\nabla^2_{R_2} \\ &= -\frac{1}{2\mu_{31}}\nabla^2_{r_3} - \frac{1}{2\mu_{31,2}}\nabla^2_{R_3}, \end{aligned} \tag{18}$$

where μ_{ij} is a reduced mass of a particle X_i and X_j and $\mu_{ij,k}$ is a reduced mass of particles (X_i, X_j) and a particle X_k. ∇_{r_c} is a differential operator of coordinate $\mathbf{r}_c$ and analogously for ∇_{R_c}.

We express a three-body wavefunction of a state having total angular momentum J and its projection onto z-axis M by a linear combination of functions written in these Jacobian coordinate systems,

$$\Psi_{JM} = \sum_c \Phi^{(c)}_{JM}(\mathbf{r}_c, \mathbf{R}_c). \tag{19}$$

The amplitude $\Phi^{(c)}_{JM}(\mathbf{r}_c, \mathbf{R}_c)$ is expanded by Gaussian functions and spherical harmonics,

$$\Phi^{(c)}_{JM}(\mathbf{r}_c, \mathbf{R}_c) = \sum_{i=1}^{n_c}\sum_{l_c}\sum_{j=1}^{N_c}\sum_{L_c} C_{cil_cjL_c} r_c^{l_c} R_c^{L_c} \exp\left(-a_i r_c^2 - A_j R_c^2\right)\left[Y_{l_c}(\hat{\mathbf{r}}_c) \otimes Y_{L_c}(\hat{\mathbf{R}}_c)\right]_{JM}, \tag{20}$$

where l_c and L_c are angular momenta for expansion (or called inner angular momenta in the present thesis) and the angular part of the wavefunction is defined as

$$\left[Y_l(\hat{\mathbf{r}}) \otimes Y_L(\hat{\mathbf{R}})\right]_{JM} \equiv \sum_{m_l}\sum_{m_L} C(lm_l Lm_L|JM) Y_{lm_l}(\hat{\mathbf{r}}) Y_{Lm_L}(\hat{\mathbf{R}}) \tag{21}$$

$C(l_1 m_1 l_2 m_2 | l_3 m_3)$ is the Clebsch-Gordan coefficient. Non-linear coefficients a_i and A_i are given in geometric progression as

$$a_i = 1/\tilde{a}_i^2, \qquad \tilde{a}_i = \tilde{a}_{\rm min} p_a^{i-1}, \tag{22}$$

$$A_j = 1/\tilde{A}_j^2, \qquad \tilde{A}_j = \tilde{A}_{\rm min} p_A^{j-1}. \tag{23}$$

p_a and p_A are common ratios and $\tilde{a}_i$ and $\tilde{A}_j$ are called Gaussian range parameters. We can optimize the minimum/maximum range of these parameters together with the number of functions. Basically the Gaussian ranges and the number of functions also depend on c, l_c and L_c though the notation is omitted for simplicity here. Linear coefficients $C_{cil_cjL_c}$ are determined from the Rayleigh-Ritz variational principle by solving the Schrödinger equation $(H_3 - E)\Psi_{JM} = 0$ with conditions

$$\left\langle \Psi^{(\upsilon')}_{JM} \middle| \Psi^{(\upsilon)}_{JM} \right\rangle = \delta_{\upsilon'\upsilon}, \tag{24}$$

and

$$\left\langle \Psi^{(\upsilon')}_{JM} \middle| H_3 \middle| \Psi^{(\upsilon)}_{JM} \right\rangle = E_\upsilon \delta_{\upsilon'\upsilon}, \tag{25}$$

where $\Psi^{(\upsilon)}_{JM}$ is υ-th eigenfunction and E_υ is its corresponding eigenenergy. Since the basis functions are not orthogonal each other, the Schrödinger equation can be transformed to a generalized eigenvalue

problem. The Gaussian basis functions allow us to calculate the matrix elements of the generalized eigenvalue problem analytically free from the choice of coordinate systems and even for complicated operators, which is also an advantage of GEM.

Treatment of 4-body system is essentially based on the same idea. For a system consisting of four particles X_1, X_2, X_3 and X_4 interacting each other via central forces, the Hamiltonian is written as

$$H_4 = K_1 + K_2 + K_3 + K_4 - K_{\rm CM} + V_{12} + V_{13} + V_{14} + V_{23} + V_{24} + V_{34}. \tag{26}$$

Jacobian coordinate systems of the 4-body system are shown in Fig. 4. The kinetic operators written in a Jacobian coordinate system $c = 1$ is

$$K_1 + K_2 + K_3K_4 - K_{\rm CM} = -\frac{1}{2\mu_{12}}\nabla^2_{r_1} - \frac{1}{2\mu_{12,3}}\nabla^2_{R_1} - \frac{1}{2\mu_{123,4}}\nabla^2_{\rho_1}. \tag{27}$$

The kinetic operators in other coordinate systems can be written in a similar way.

A four-body wavefunction of a state having total angular momentum J and its projection onto z-axis M is expressed by a linear combination of functions written in these Jacobian coordinate systems,

$$\Psi_{JM} = \sum_c \Phi^{(c)}_{JM}(\mathbf{r}_c,\, \mathbf{R}_c,\, \boldsymbol{\rho}_c). \tag{28}$$

The amplitude $\Phi^{(c)}_{JM}(\mathbf{r}_c,\, \mathbf{R}_c,\, \boldsymbol{\rho}_c)$ is expanded by Gaussian functions and spherical harmonics,

$$\begin{aligned}\Phi^{(c)}_{JM}(\mathbf{r}_c,\, \mathbf{R}_c,\, \boldsymbol{\rho}_c) = &\sum_{i=1}^{n_c}\sum_{l_c}\sum_{j=1}^{N_c}\sum_{L_c}\sum_{k=1}^{\nu_c}\sum_{\lambda_c}\sum_{\Lambda_c} C_{cil_cjL_ck\lambda_c\Lambda_c} r_c^{l_c} R_c^{L_c} \rho_c^{\lambda_c} \exp\left(-a_i r_c^2 - A_j R_c^2 - \alpha_k \rho_c^2\right) \\ &\times \left[\left[Y_{l_c}(\hat{\mathbf{r}}_c) \otimes Y_{L_c}(\hat{\mathbf{R}}_c)\right]_{\Lambda_c} \otimes Y_{\lambda_c}(\hat{\boldsymbol{\rho}}_c)\right]_{JM},\end{aligned} \tag{29}$$

where l_c, L_c and λ_c are angular momenta for expansion and the angular part of the wavefunction is defined as

$$\begin{aligned}&\left[\left[Y_l(\hat{\mathbf{r}}) \otimes Y_L(\hat{\mathbf{R}})\right]_{\Lambda} \otimes Y_\lambda(\hat{\boldsymbol{\rho}})\right]_{JM} \\ &\equiv \sum_{m_\Lambda}\sum_{m_\lambda}\sum_{m_l}\sum_{m_L} C(\Lambda m_\Lambda \lambda m_\lambda | JM) C(l m_l L m_L | \Lambda m_\Lambda) Y_{lm_l}(\hat{\mathbf{r}}) Y_{Lm_L}(\hat{\mathbf{R}}) Y_{\lambda m_\lambda}(\hat{\boldsymbol{\rho}}).\end{aligned} \tag{30}$$

The summation of Λ_c runs over all possible angular momenta composed of l_c and L_c.

Non-linear coefficients a_i, A_i are given in geometric progression as in the case of three-body system. Linear coefficients $C_{cil_cjL_ck\lambda_c}$ are determined from the Rayleigh-Ritz variational principle by solving the Schrödinger equation $(H_4 - E)\Psi_{JM} = 0$. Unlike the three-body calculation, evaluation of the matrix elements of four-body system becomes complicated even using Gaussian functions. Infinitesimally-shifted Gaussian basis functions can be used to the analytical evaluation of the matrix elements. A product of the radial part Gaussian function and angular part spherical harmonics can be expanded in finite number of infinitesimally-shifted Gaussian functions as

$$r^l \exp(-ar^2) Y_{lm}(\hat{\mathbf{r}}) = \lim_{\epsilon\to 0} \frac{1}{\epsilon^l} \sum_{\kappa=1}^{\kappa_{\rm max}} C_{lm,\kappa} \exp\left[-a(\mathbf{r} - \epsilon \mathbf{D}_{lm,k})^2\right], \tag{31}$$

where parameters $C_{lm,\kappa}$ and $\mathbf{D}_{lm,k}$ are not unique but can be chosen arbitrarily and the relationship between them can be determined analytically. Since the infinitesimally-shifted Gaussian function does not have spherical harmonics explicitly, the evaluation of the matrix elements becomes simple.

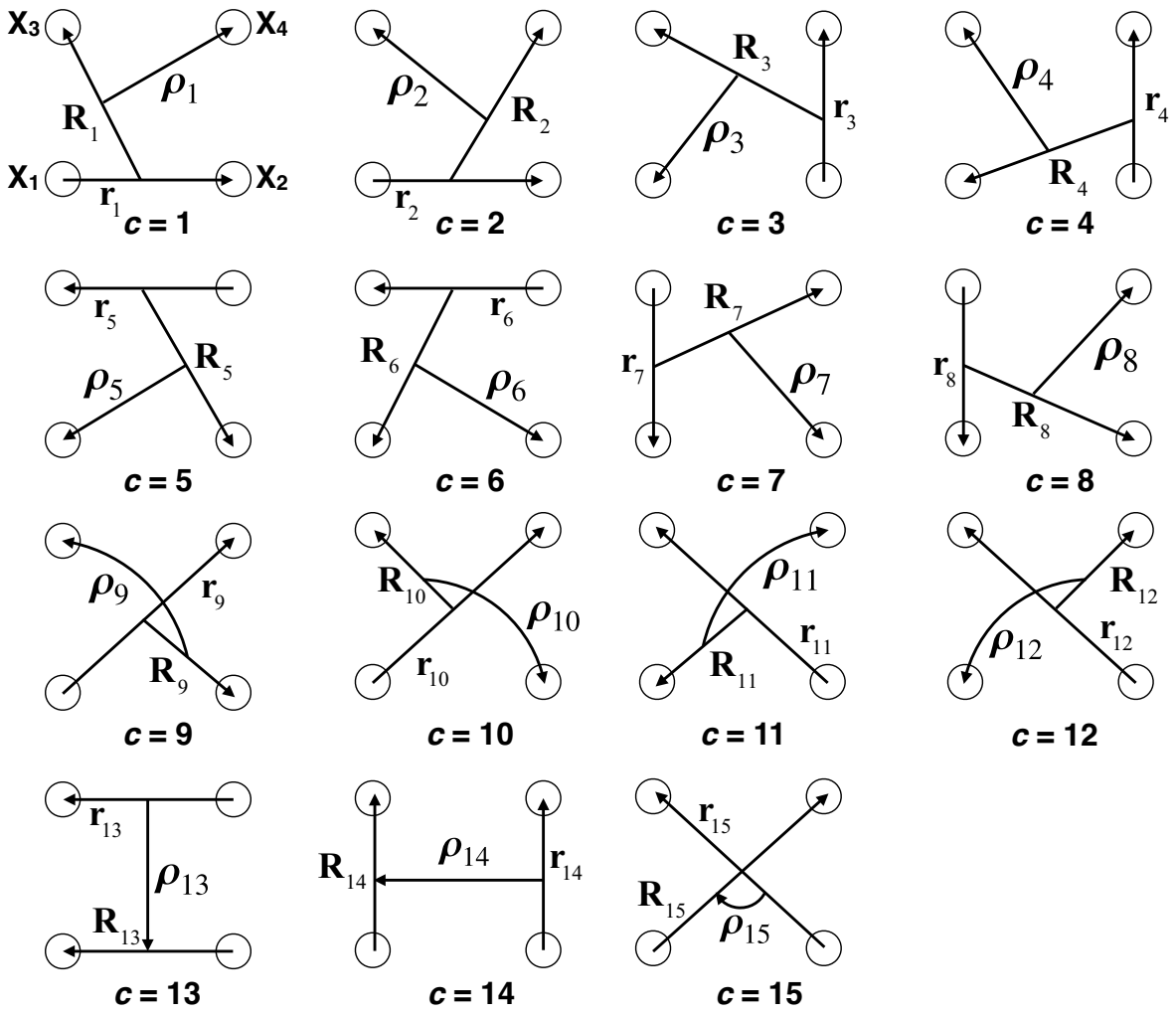

Figure 4: Jacobian coordinate systems for a 4-body system consisting of X_1, X_2, X_3 and X_4.

Chapter 3 Positronic atom

This chapter describes theoretical investigations into loosely bound states of positronic alkali atoms and their resonance states. Relativistic effects on the loosely bound states of $LiPs^+$ and $NaPs^+$ are evaluated and the difference of the role of the relativistic effects among positronic atoms and ordinary atomic systems is discussed in section 3-1. A three-body correlation, or channel coupling effect, among a positron, a valence electron and an ion in bound and resonance states are examined for various positronic alkali atoms together with positronic copper atom in section 3-2.

The positron-atom interaction has been studied so far and it has been known that a positron and a neutral atom can form a bound state called positronic atom. The positron cannot penetrate into the atom because of the repulsion from the nucleus. On the other hand, the positron outside the atom feels an attractive potential caused by induced dipole interaction. Therefore, the positron can make a bond with the atom, and distributes broadly around the atom as shown in Fig. 5 (a). A bound state of a positron and an atom is called a positronic atom. Since the positron can form a positronium (Ps; a hydrogen-like atom conisting of e^- and e^+) with an electron, the positron associating with an atom can capture one of the electrons in the atom, and can form a positronium virtually as shown in Fig. 5 (b). The virtual positronium formation in the positronic atom can also be interpreted as neutralization of electron, which is a unique aspect of the positron-atom interaction. Although the bound state of positron and an atom cannot be stable against annihilation, the uncertainty of energy caused from the finite lifetime becomes 10^{-6} eV which is much smaller than typical binding energy of the positronic atoms, about 10^{-2} eV.

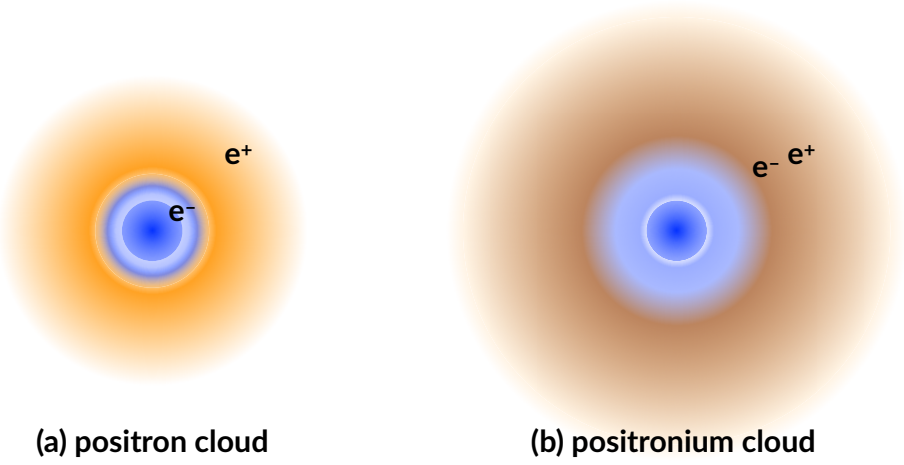

Figure 5: Cross section of schematic picture of positronic atoms. The blue region draws electron cloud and orange region draws positron cloud. An electron cloud of the inner core ion is covered with (a) positron or (b) positronium cloud.

3-1 Loosely bound states and relativistic effects

As pointed out in a number of previous calculations [19–33], the major binding mechanism for a positronic alkali atom is Ps polarization by the positive ion core. When a positron attaches to an alkali atom (A), the valence electron transfers to the positron and forms Ps because the ionization energies of alkali atoms ($\sim$ 5 eV) are smaller than the binding energy of Ps (6.8 eV). The residual ion core polarizes the Ps and forms a loosely bound state of the positronic alkali atom (APs^+) just below the A^++Ps threshold energy. Bound states of a positronic lithium atom ($LiPs^+$) and positronic sodium atom ($NaPs^+$) have been predicted theoretically, and positronic potassium or heavier alkali atoms have been considered not to have any bound state [33].

Relativistic effects in atomic/molecular systems have recently received attention, and various studies have been conducted because such effects dramatically change the characteristics of heavy atoms from non-relativistic prediction. The major interests of relativistic atomic physics and quantum chemistry are spin-forbidden chemical reactions, unique structures of compounds, and electronic states involving spin-orbit coupling (see [34, 35] and references therein). In these studies, 6th- and 7th-period elements have often been the subject of research. Relativistic corrections to the binding energy of positronic alkali atoms, however, have been considered to be unimportant because of the small atomic numbers of Li and Na. Some of the exhaustive investigations for e^+/Ps-atom complexes within relativistic frameworks were described by Saito [36] and Harabati *et al.* [37].

In the present study, relativistic corrections for positronic alkali atoms are calculated up to α^2 order, where α is the fine structure constant. The binding energy by high-precision calculations with a relativistic framework is reported and the roles of the relativistic effect in the ground state is examined based on the decomposed expectation values of the perturbation Hamiltonian for the relativistic effect.

Contents of this section are developed based on parts of the following published works:

- Takuma Yamashita, Ayumi Irisawa, and Yasushi Kino, "Estimation of relativistic effects on loosely bound states of positronic alkali atoms", Japanese Journal of Applied Physics Conference Proceedings **2**, 011005 (2014).
- Takuma Yamashita, Yasushi Kino, "High-precision calculation of loosely bound states of $LiPs^+$ and $NaPs^+$", Journal Physics: Conference Series **618**, 012009 (2015).
- Takuma Yamashita, Yasushi Kino, "Relativistic effects in positronic alkali atoms", Journal Physics: Conference Series **635**, 052086 (2015).
- 木野康志, 山下琢磨,「陽電子が拓く物質の科学 第 2 回 陽電子・原子間相互作用と陽電子原子」, 原子衝突学会誌「しょうとつ」 **13**, 37 (2016).
- 山下琢磨, 木野康志,「相対論効果を含む陽電子アルカリ原子の弱束縛状態の高精度計算」, 日本陽電子科学会誌「陽電子科学」 **6**, 35 (2016).

Method

The non-relativistic three-body Hamiltonian is given by

$$H^{\rm nr}_{\rm APs^+} = -\frac{1}{2}\nabla^2_{\rm e} - \frac{1}{2}\nabla^2_{\rm p} + V^{\rm nr}_{\rm e}(r_{\rm e}) + V^{\rm nr}_{\rm p}(r_{\rm p}) - \frac{1}{r_{\rm ep}} + V_{\rm 2pol}(\mathbf{r}_{\rm e}, \mathbf{r}_{\rm p}) + \lambda \sum_i |\phi^{\rm core}_i\rangle\langle\phi^{\rm core}_i|, \tag{32}$$

where $V_{\rm 2pol}$ is a two-body correction to the polarization potentials for the electron and positron [38]. A coordinate $\mathbf{r}_{\rm e}$ is a vector sees the electron from the nucleus, $\mathbf{r}_{\rm e}$ is a vector sees the positron from the nucleus, $\mathbf{r}_{\rm ep}$ is a vector sees the electron from the positron. The model potential $V^{\rm nr}_{\rm e}$ is constructed to reproduce atomic energy levels including relativistic corrections on the valence electron and $V^{\rm nr}_{\rm p}$ can be constructed from the components of $V^{\rm nr}_{\rm e}$. The last term of the Hamiltonian (32) is introduced in order to remove pseudo states, in which the electron occupies a core orbital $\phi^{\rm core}_i$, from the total wavefunction [39]. By using a Gaussian expansion method (GEM), the three-body bound state wavefunction Ψ in S-state is expanded in terms of channel functions as

$$\Psi = \Phi^{(c=1)}(\mathbf{r}_{\rm ep}, \mathbf{R}) + \Phi^{(c=2)}(\mathbf{r}_{\rm e}, \mathbf{r}_{\rm p}). \tag{33}$$

The first function is expanded in terms of Gaussian basis functions and spherical harmonics written in a coordinate system ($\mathbf{r}_{\rm e}$, $\mathbf{r}_{\rm e}$) and the second function in another coordinate system ($\mathbf{r}_{\rm ep}$, $\mathbf{R}$) where $\mathbf{R}$ is a vector sees the center-of-mass of Ps from the nucleus.

A perturbation Hamiltonian for relativistic corrections is based on the Breit-Pauli interactions [40, 41] and is written as

$$H^{\rm rel}_{\rm APs^+} = H'_{\rm mv} + H'_{\rm D} + H'_{\rm ret} + H'_{\rm ss} + H'_{\rm a}, \tag{34}$$

$H'_{\rm mv}$ is a relativistic momentum correction, $H'_{\rm D}$ is the Darwin term, $H'_{\rm ret}$ is the retardation correction, $H'_{\rm ss}$ is the spin-spin interaction, and $H'_{\rm a}$ is a correction from the annihilation channel. The relativistic correction regarding the nucleus spin can be neglected because the magnetic moment of the nucleus is three orders of magnitude smaller than that of the electron. There could be a spin-orbit interaction; however, the loosely bound state with $J = 0$ cannot be contributed from the spin-orbit interaction. The total relativistic correction $\Delta\varepsilon^{\rm rel}$ is calculated by the first-order perturbation theory:

$$\Delta E^{\rm rel}_{\rm APs^+} = \alpha^2\langle H^{\rm rel}_{\rm APs^+}\rangle = \alpha^2\langle\Psi \mid H^{\rm rel}_{\rm APs^+} \mid \Psi\rangle. \tag{35}$$

Results and discussion

The present work reports that the difference between "relativistic binding energy" and "non-relativistic binding energy" of $LiPs^+$ ($NaPs^+$) becomes drastically large in compared with the difference between them of Li (Na) and also of Li^- (Na^-). Based on an analysis of decomposed relativistic corrections, it is found that the characteristic role of relativistic effects in loosely bound states of positronic lithium/sodium atoms is supported by two major correlations: the one is nucleus-electron correlation hidden in a major structure of the bound state and the other is positron-electron correlation remarkable in the major structure. In the asymptotic region, the charge of the valence electron is screened by the positron. In

other words, a cancellation of the long-range non-relativistic potentials occurs, which results in a small binding energy. Near the nucleus, the electron is released from the positron and is subject to significant relativistic effects. The transformation of these structures in a single quantum state is, in other words, spontaneous rearrangement of the valence electron between the nucleus and positron. Unlike ordinary molecules, the positronic atom does not hold a rigid architecture due to positron's light mass; however, the electron and a positron are equivalent constituents of the positronic atom in a view of their equivalent masses. Thus, the electron transfer between the nucleus and positron may be interpreted as the analogy or extension of the spontaneous rearrangement though usually the word spontaneous rearrangement is used to describe the change of nuclear positions leading the change of the molecular framework. The present result emphases the importance of the relativistic effect in positronic atoms of light elements.

3-2 Resonance states and channel-coupling effects

This section focuses on resonance states of positronic atoms. In particular, resonance states belonging to "dipole series" in positronic alkali atoms are investigated. The dipole series which rises from a permanent dipole moment of an excited Ps induced by an electric field of an ion has been identified in e^+H, e^+He ($^3S^e$) and e^+Li [42–44]. Calculations of the dipole series require an accurate method to describe broadly-distributed wavefunction of Ps, typically a few hundred atomic units [45–47].

The formation mechanism of the resonance states must be affected by dissociation thresholds located close to the resonance. The present work performs calculations on resonance states of positronic lithium/copper atoms and a systematic coupled channel three-body study on resonance states of positronic alkali atoms (e^+A; A=Li, Na, K, Rb and Cs) to investigate characteristics of the dipole series of resonance states in positronic atoms. A channel coupling effect on the resonance states in the dipole series, namely their plural association to atomic orbitals are focused. How the resonance states are associated with the atomic energy levels and how the electron is associated with the positron and ion are discussed.

Contents of this subsection have been published in:

- Takuma Yamashita and Yasushi Kino, "Calculation of resonance states of positronic lithium atom", Eur. Phys. J. D **70**, 190 (2016).
- Takuma Yamashita, Muhammad Umair and Yasushi Kino, "Bound and resonance states of positronic copper atoms", J. Phys. B: At. Mol. Opt. Phys. **50**, 205002 (2017).
- Takuma Yamashita and Yasushi Kino, "Coupled channel effects on resonance states of positronic alkali atom", Eur. Phys. J. D **72**, 13 (2018).

Dipole series

Dipole series is caused by an electric field of alkali ion. Ps ($n = 2$) has four degenerated states $\psi_{nlm}(r, \theta, \phi)$, in which (nlm) =(200), (210), (211), (21−1). We assume that a static electric field **F**,

which is directed along the z-axis, is on a positronium. The perturbation Hamiltonian H'_F is written as

$$H'_F = e\mathbf{F}\cdot\mathbf{r} = eFr\cos\theta. \tag{36}$$

Since the H'_F is an *odd* operator, an integral with the same states vanishes,

$$\langle\psi_{nlm}|H'_F|\psi_{nlm}\rangle = 0. \tag{37}$$

Thus, non-vanishing matrix elements come from integrals between the states (200) and (210). Eigenstates of this perturbation Hamiltonian are sp-hybridization states

$$\psi_1 = \frac{1}{\sqrt{2}}\left(\psi_{200} + \psi_{210}\right), \tag{38}$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left(\psi_{200} - \psi_{210}\right), \tag{39}$$

$$\psi_3 = \psi_{211}, \tag{40}$$

$$\psi_4 = \psi_{21-1}. \tag{41}$$

Since these eigenstates do not depend on the strength of the electric field F, Ps ($n = 2$) state has a permanent electric dipole moment even in a weak external electric field. Thus, ion-Ps ($n = 2$) interaction might be described in ion-dipole interaction proportional to r^{-2}. This long range potential generates an infinite sequence of quasi bound states, in principle. The binding energies of each sequence follow a simple analytical low [48],

$$\ln\varepsilon_\upsilon = -\sigma\upsilon + \text{const.}, \tag{42}$$

where

$$\sigma = \frac{2\pi}{\sqrt{(2J+1)\left[\sqrt{\left(\frac{6\mu_{\mathrm{A}^+,\mathrm{ep}}}{\mu_{\mathrm{ep}}(2J+1)}\right)^2+1}-1-\left(J-\frac{1}{2}\right)\right]}}. \tag{43}$$

Here, μ_{ep} is a reduced mass of the electron and positron and $\mu_{\mathrm{A}^+,\mathrm{ep}}$ is a reduced mass of the alkali ion and Ps. The $\sigma = 1.317$ is a unique parameter of Ps ($n = 2$) and υ is a vibrational quantum number.

Method

A Hamiltonian for the three-body system $\mathrm{e}^+\mathrm{A}$ consisting of an electron, an ion A^+ and a positron is given as

$$H_{\mathrm{e}^+\mathrm{A}} = -\frac{1}{2}\nabla^2_{r_\mathrm{e}} - \frac{1}{2}\nabla^2_{r_\mathrm{p}} + V^{\mathrm{A}}_{\mathrm{e}}(r_\mathrm{e}) + V^{\mathrm{A}}_{\mathrm{p}}(r_\mathrm{p}) - \frac{1}{r_{\mathrm{ep}}} + V_{2\mathrm{pol}}(\mathbf{r}_\mathrm{e},\mathbf{r}_\mathrm{p}). \tag{44}$$

where $V^{\mathrm{A}}_{\mathrm{e}}$ ($V^{\mathrm{A}}_{\mathrm{p}}$) are a model potential between the electron (positron) and the ion, $V_{2\mathrm{pol}}(\mathbf{r}_\mathrm{e},\mathbf{r}_\mathrm{p})$ is a two-body correction to the polarization effect. In a similar way as the calculation of loosely bound state, the total three-body wavefunction is expanded in terms of channel functions:

$$\Psi = \Phi^{(c=1)}(\mathbf{r}_{\mathrm{ep}},\mathbf{R}) + \Phi^{(c=2)}(\mathbf{r}_\mathrm{e},\mathbf{r}_\mathrm{p}). \tag{45}$$

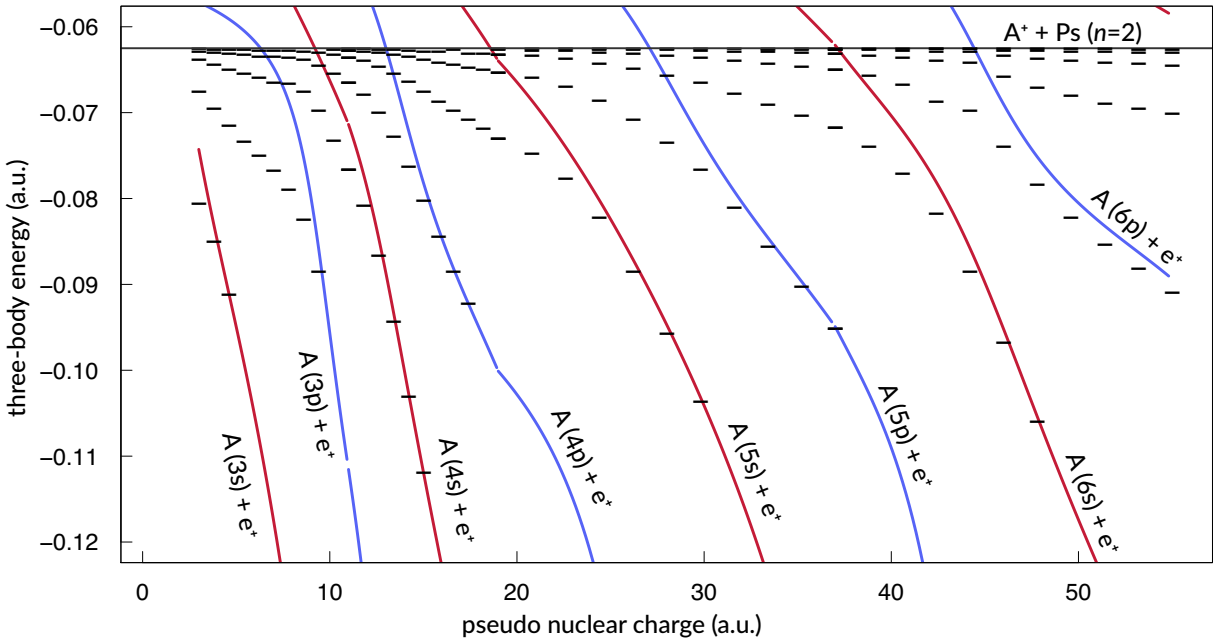

Figure 6: Resonance energies are shown by black lines against the pseudo nuclear charge. Red curves are thresholds of A (ns) + e^+ whose energy is given by the model potential Eq. (48). Blue curves are thresholds of A (np) + e^+ whose energy is given by the model potential Eq. (48). A horizontal black line is the threshold of A^+ + Ps (n = 2).

The first function is expanded in terms of Gaussian basis functions and spherical harmonics written in a coordinate system ($\mathbf{r}_e$, $\mathbf{r}_e$) and the second function in another coordinate system ($\mathbf{r}_{ep}$, $\mathbf{R}$) where $\mathbf{R}$ is a vector sees the center-of-mass of Ps from the nucleus.

Resonance energies and widths are determined by a real scaling method for positronic lithium atom and a complex scaling method [49] for positronic copper atom and for other positronic alkali atoms. A complex scaled Schrödinger equation is given by

$$\mathcal{U}(\theta)H\mathcal{U}(\theta)^{-1}\Psi_0(\theta) = E(\theta)\Psi_0(\theta), \tag{46}$$

where $\mathcal{U}(\theta)$ is a complex dilation operator, $E(\theta)$ is a complex value and $\Psi_0(\theta) = \mathcal{U}(\theta)\Psi_0$ is a complex scaled wavefunction. The resonance energy and width can be determined by the complex eigenvalue $E(\theta') = E_r - i\Gamma/2$ when

$$dE(\theta)/d\theta|_{\theta=\theta'} = 0 \tag{47}$$

is satisfied.

Results and discussion

The present works on the positronic lithium/copper atom reveal resonance energies and widths of resonance states belonging to dipole series. One of the resonance states shows a large deviation from the analytical law derived from two-body approximation and the resonance position and width show a strong

dependency on the element of the atom. In order to investigate the effect of the presence of the A + e^+ dissociation thresholds on the resonance states near the thresholds, the following pseudo potentials are introduced

$$V_{\mathrm{e}}^{\mathrm{A}-\mathrm{A}'}(r_{\mathrm{e}}; x) = xV_{\mathrm{e}}^{\mathrm{A}}(r_{\mathrm{e}}) + (1-x)V_{\mathrm{e}}^{\mathrm{A}'}(r_{\mathrm{e}}), \tag{48}$$

where $0 \leq x \leq 1$ is a parameter to connect the two alkali atoms A and A′ smoothly. This connected model potential could roughly be regarded as a model potential for a pseudo-alkali-atom A_x whose pseudo nuclear charge is $Z_x = xZ_{\mathrm{A}} + (1-x)Z_{\mathrm{A}'}$ where Z_{A} and $Z_{\mathrm{A}'}$ are atomic numbers for A and A′. Pseudo potentials between A_x^+ and e^+, $V_{\mathrm{p}}^{\mathrm{A}-\mathrm{A}'}$, are also defined in the same way. The present work calculates 40 series of resonance states among $3 \leq Z_x \leq 55$ and determines resonance energies and widths.

Figure 6 shows the resonance energies calculated by the model potentials $V_{\mathrm{e}}^{\mathrm{A}-\mathrm{A}'}$ and $V_{\mathrm{p}}^{\mathrm{A}-\mathrm{A}'}$ against the pseudo nuclear charge. While it is found that the resonance states close to A^+ + Ps ($n = 2$) threshold obey an analytical law under two-body approximation, resonance states far from the threshold and close to the atomic energy levels show a large deviation from the analytical law. One can see in Fig. 6 that the resonance positions far from the threshold A^+ + Ps ($n = 2$) are associated with the thresholds of A + e^+. When the excited positronium comes close to the ion, the two-body assumption is violated and the electron transfers to the ion. It is also found that the change of the major associated thresholds can give a longer lifetime than the expected from the two-body approximation. In other words, the resonance states in dipole series generally show a plural association with different thresholds, or hold two different structures that are connected via the spontaneous rearrangement. The resonance energies and lifetimes are affected by degree to the associations.

Chapter 4 Hydrogen anti-hydride molecule

Since an antinucleus is negatively charged and has a large mass in comparison with that of electron, on the interaction between an antinucleus and an atom, the antinucleus strongly couples with the nucleus. The antinucleus can be captured by the atom emitting electrons and then residual electrons are ionized via Auger transitions caused by the de-excitation of nucleus-antinucleus system. After all of the electrons are emitted out, the nucleus-antinucleus system further de-excites via radiative transitions. Due to the cascade process involving the Auger transitions and radiative transitions, the antinucleus-atom system cannot have a bound state.

This chapter describes theoretical studies on the hydrogen anti-hydride molecule ($H\bar{H} = pe^-\bar{p}e^+$) and its ion, antiprotonic hydrogen atom ($\bar{p}H$). $\bar{p}H$ involves a fundamental aspect of antinucleus-atom interaction, and $H\bar{H}$ involves that of matter-antimatter interaction. The aim of the present work is to seek molecular states of these systems like H_2 or H_2^+. Zygelman *et al.* [50] suggested a possibility of the $H\bar{H}$ formation in a cold collision via radiative association,

$$H + \bar{H} \to H\bar{H} + \gamma. \tag{49}$$

The collision process of $H + \bar{H}$ has been attracted attentions in both of theoretical and experimental aspects [51]. Rearrangement process and annihilation process play an indispensable role in the cold collision [52, 53].

The molecular state of $H\bar{H}$ and molecular-ion state of $\bar{p}H$ are classified to resonance states having finite lifetime against particle rearrangement dissociation. When the relative distance between the proton and antiproton becomes long in the molecular resonance state, the rearrangement dissociation may be suppressed and the lifetime of such state can be prolonged. Although historically these states have been investigated based on adiabatic approximations [54–56], non-adiabatic treatment which can deal with the decaying process of the resonance state is indispensable for further studies. The present work performs a non-adiabatic calculation of resonance states of $\bar{p}H$ and $H\bar{H}$ by using Gaussian expansion method with a complex coordinate rotation method. Resonance states located below $H + \bar{H}$ / $\bar{p} + H$ threshold are searched and the stability against the rearrangement dissociation and annihilation is examined.

Contents of this chapter are developed based on parts of the following published works:

- Takuma Yamashita and Yasushi Kino, "Three-body resonance states just below the antiproton and hydrogen dissociation threshold", Eur. Phys. J. Web Conf. **181**, 01034 (2018).
- Takuma Yamashita and Yasushi Kino, "Coupled channel study of antihydrogen-hydrogen molecular resonance state", JJAP Conf. Proc. **7**, 011004 (2018).

Method

A total Hamiltonian of $\bar{p}H$ is written as

$$H_{\bar{p}H} = \hat{K}_{\bar{p}} + \hat{K}_p + \hat{K}_{e^-} - \hat{K}_{CM} - \frac{1}{r_{pe^-}} + V_{\bar{p}p}(r_{\bar{p}p}) + \frac{1}{r_{\bar{p}e^-}}, \tag{50}$$

where $\hat{K}_{\rm x}$ (x = {$\bar{\rm p}$, p, e^-}) is a kinetic energy operator associated with position vector of particle x, $\hat{K}_{\rm CM}$ is the kinetic energy operator for center of mass of the system and $r_{\rm xy}$ is relative distance between particle x and y. The mass of proton and antiproton is set to be $m_{\rm p}(m_{\bar{\rm p}}) = 1836.152\,673\,89$. $V_{\bar{\rm p}{\rm p}}$ describes interaction between the proton and antiproton. The $V_{\bar{\rm p}{\rm p}}$ must involve not only Coulomb interaction but also strong nuclear force and quark rearrangement process resulting in annihilation. In the present work, we first consider only the Coulomb potential, $V_{\bar{\rm p}{\rm p}} = -1/r_{\bar{\rm p}{\rm p}}$, and then we evaluate the effects of the strong nuclear force and quark rearrangement process on the results obtained by the Coulomb potential. Similarly, a total Hamiltonian of H$\bar{\rm H}$ is written as

$$H_{\rm H\bar{H}} = \hat{K}_{\bar{\rm p}} + \hat{K}_{\rm p} + \hat{K}_{e^-} + \hat{K}_{e^+} - \hat{K}_{\rm CM} - \frac{1}{r_{{\rm p}e^-}} + V_{\bar{\rm p}{\rm p}}(r_{\bar{\rm p}{\rm p}}) - \frac{1}{r_{\bar{\rm p}e^+}} - \frac{1}{r_{e^-e^+}} + \frac{1}{r_{\bar{\rm p}e^-}} + \frac{1}{r_{{\rm p}e^+}}. \tag{51}$$

The definitions of $\hat{K}_{\bar{\rm x}}$ is the same as in Eq. (50). In the same way as $\bar{\rm p}$H, we first consider a Coulomb potential for $V_{\bar{\rm p}{\rm p}}$ and then $V_{\bar{\rm p}{\rm p}}$ is extended to include strong nuclear potential and annihilation effects.

A wavefunction of $\bar{\rm p}$H having total angular momentum J and its projection onto z-axis M is expanded in terms of a radial Gaussian function and a bipolar spherical harmonics $\mathcal{Y}^{(JM)}_{l_c L_c}$ written in several coordinate systems as

$$\Psi^{(JM)}_{\bar{\rm p}{\rm H}} = \sum_c \sum_i A_{ci} \mathcal{G}^{l_{ci}L_{ci}}_{ci}(r_c, R_c) \mathcal{Y}^{(JM)}_{l_{ci}L_{ci}}(\hat{\mathbf{r}}_c, \hat{\mathbf{R}}_c), \tag{52}$$

where a coordinate system c is defined by a set of coordinates ($\mathbf{r}_c$, $\mathbf{R}_c$), and the radial Gaussian function is written in $\mathcal{G}^{l_{ci}L_{ci}}_{ci}(r_c, R_c) = r_c^{l_{ci}} R_c^{L_{ci}} \exp(-a_{ci} r_c^2 - A_{ci} R_c^2)$. l_{ci} and L_{ci} are inner angular momentum quantum numbers which specify the order of the bipolar spherical harmonics. The present work introduces three coordinate systems $c = 1$, 2 and 3. In the first coordinate system $c = 1$ consisting of a set of coordinates ($\mathbf{r}_1$, $\mathbf{R}_1$), a vector $\mathbf{r}_1$ sees e^- from p and a vector $\mathbf{R}_1$ sees $\bar{\rm p}$ from p. In the second coordinate system $c = 2$ consisting of a set of coordinates ($\mathbf{r}_2$, $\mathbf{R}_2$), a vector $\mathbf{r}_2$ sees e^- from the center-of-mass of the pair (p, $\bar{\rm p}$) and a vector $\mathbf{R}_2$ is equivalent to $\mathbf{R}_1$. In the third coordinate system $c = 3$ consisting of a set of coordinates ($\mathbf{r}_3$, $\mathbf{R}_3$), a vector $\mathbf{r}_3$ sees e^- from $\bar{\rm p}$ and a vector $\mathbf{R}_3$ sees p from $\bar{\rm p}$. The coordinate system $c = 1$ is suitable to describe a bond between the antiproton and hydrogen atom, and $c = 2$ is suitable to describe motion of the electron dissociating from protonium. $c = 3$ is an auxiliary coordinate system that helps the description of repulsive inter-particle correlations.

Similarly as $\Psi^{(JM)}_{\bar{\rm p}{\rm H}}$, a wavefunction of H$\bar{\rm H}$ having total angular momentum J and its projection onto z-axis M is expanded as

$$\Psi^{(JM)}_{\rm H\bar{H}} = \sum_c \sum_i A_{ci} \mathcal{G}^{l_{ci}L_{ci}\lambda_{ci}}_{ci}(r_c, R_c\,\rho_c) \mathcal{Y}^{(JM)}_{l_{ci}L_{ci}\lambda_{ci}}(\hat{\mathbf{r}}_c, \hat{\mathbf{R}}_c, \hat{\boldsymbol{\rho}}_c), \tag{53}$$

where a coordinate system c is defined by a set of coordinates ($\mathbf{r}_c$, $\mathbf{R}_c$, $\boldsymbol{\rho}_c$) and the radial Gaussian function is written in $\mathcal{G}^{l_{ci}L_{ci}\lambda_{ci}}_{ci}(r_c, R_c, \rho_c) = r_c^{l_{ci}} R_c^{L_{ci}} \rho_c^{\lambda_{ci}} \exp(-a_{ci} r_c^2 - A_{ci} R_c^2 - \alpha_{ci} \rho_c^2)$. l_{ci}, L_{ci} and λ_{ci} are inner angular momentum quantum numbers which specify the order of the tripolar spherical harmonics $\mathcal{Y}^{(JM)}_{l_{ci}L_{ci}\lambda_{ci}}$.

We construct the resonance wavefunction of H$\bar{\rm H}$ to include a configuration describing a structure that the hydrogen atom and antihydrogen atom orbits around each other, together with a configuration describing rearrangement dissociation state Pn + Ps. For this aim, three coordinate systems are introduced. In the first coordinate system $c = 1$ consisting of a set of coordinates ($\mathbf{r}_1$, $\mathbf{R}_1$, $\boldsymbol{\rho}_1$), the vector

$\mathbf{r}_1$ sees e^+ from $\bar{p}$, $\mathbf{R}_1$ sees p from $\bar{p}$, and $\boldsymbol{\rho}_1$ sees e^- from p. In the second coordinate system $c = 2$ consisting of a set of coordinates ($\mathbf{r}_2$, $\mathbf{R}_2$, $\boldsymbol{\rho}_2$), the vector $\mathbf{r}_2$ sees e^+ from e^-, $\mathbf{R}_2$ is equivalent with $\mathbf{R}_1$, and $\boldsymbol{\rho}_2$ sees the center-of-mass of a pair (e^+, e^-) from the center-of-mass of a pair (p, $\bar{p}$). In the third coordinate system $c = 3$ consisting of a set of coordinates ($\mathbf{r}_3$, $\mathbf{R}_3$, $\boldsymbol{\rho}_3$), the vector $\mathbf{r}_3$ sees e^- from $\bar{p}$, $\mathbf{R}_3$ is equivalent with $\mathbf{R}_1$, and $\boldsymbol{\rho}_3$ sees e^+ from p. The coordinate system $c = 1$ is suitable to describe a bond between the hydrogen atom and antihydrogen atom, and $c = 2$ is suitable to describe motion of the positronium dissociating from protonium. $c = 3$ is an auxiliary coordinate system that helps the description of repulsive inter-particle correlations.

The linear coefficient A_{cj} in Eq. (52) is determined by the complex coordinate rotation method so that the Schrödinger equation satisfies

$$\mathcal{U}(\theta)H_{\bar{p}H}\mathcal{U}^{-1}(\theta)\mathcal{U}(\theta)\Psi^{(00)}_{\bar{p}H(\upsilon)} = E_{\bar{p}H(\upsilon)}(\theta)\mathcal{U}(\theta)\Psi^{(00)}_{\bar{p}H(\upsilon)} \tag{54}$$

where $\bar{p}H(\upsilon)$ denotes the υ-th eigenstate of $\bar{p}H$. Similarly, the linear coefficient A_{cj} in Eq. (53) is determined by the following Schrödinger equation,

$$\mathcal{U}(\theta)H_{H\bar{H}}\mathcal{U}^{-1}(\theta)\mathcal{U}(\theta)\Psi^{(00)}_{H\bar{H}(\upsilon)} = E_{H\bar{H}(\upsilon)}(\theta)\mathcal{U}(\theta)\Psi^{(00)}_{H\bar{H}(\upsilon)} \tag{55}$$

where $H\bar{H}(\upsilon)$ denotes the υ-th eigenstate of $H\bar{H}$. After the complex scaling, eigenenergies for the bound states does not change, but those for continuum states rotate θ on the dissociation threshold point in the complex energy plane. For a resonance state which has aspects of both bound and scattering states, the eigenenergy firstly rotates and then reaches a stationary point. The resonance energy E_r and width Γ are determined as $E(\theta') = E_r - i\Gamma/2$ when

$$\left.\frac{\partial E(\theta)}{\partial\theta}\right|_{\theta=\theta'} \approx 0 \tag{56}$$

is satisfied.

Results and discussion

The number and ranges of the radial Gaussian functions $\mathcal{G}_{ci}^{l_{ci}L_{ci}}$ in Eq. (52) and $\mathcal{G}_{ci}^{l_{ci}L_{ci}\lambda_{ci}}$ in Eq. (53) are optimized so that the wavefunction and energy of the fragment atoms, $\bar{H}$, H, Pn and Ps, are reproduced in convincing accuracy. Resonance states of $\bar{p}H$ just below $\bar{p}$ + H (1s) dissociation threshold can dissociate into Pn ($n \leq 30$) + e^-. Similarly, resonance states of $H\bar{H}$ just below H (1s) + $\bar{H}$ (1s) dissociation threshold can dissociate into Pn ($n \leq 24$) + Ps. The determination of the resonance energy could be sensitive to the reproducibility of the energies of $\bar{H}$ and H which affects the position of threshold H (1s) + $\bar{H}$ (1s) when the resonance is located close to the threshold. The accuracy of energies of Pn and Ps can affect the resonance widths, namely the lifetime of the resonances. Thus, thresholds Pn ($n \leq 30$) + e^- and $\bar{p}$ + H (1s) for $\bar{p}H$ and thresholds Pn ($n \leq 24$) + Ps and H (1s) + $\bar{H}$ (1s) should be reproduced. The present work also utilizes the Born-Oppenheimer (BO) calculation of $\bar{p}H$ and $H\bar{H}$ for the optimization of the number of basis functions and their ranges for the motion between proton and antiproton written in $c = 1$.

By increasing the components of the wavefunctions Eq. (52) and Eq. (53), resonance energies and widths are calculated. For $\bar{\mathrm{p}}$H, the present work have found 5 resonance states below $\bar{\mathrm{p}}$ + H (1s) dissociation threshold. Four of the resonance states show a good agreement with the previous calculation [57] by a Rmatirx method which is also the non-adiabatic approach. The previous work [57] calculated Pn + e^- scattering states and extracted the resonance energies and widths from time-delay matrix. The present work reports another resonance state located just below the $\bar{\mathrm{p}}$ + H (1s) dissociation threshold by 0.000 000 5 hartree. For H$\bar{\mathrm{H}}$, the present work reports a resonance state and a possible resonance state below H (1s) + $\bar{\mathrm{H}}$ (1s) dissociation threshold. The former resonance state shows a good convergence against the increase of the inner angular momenta while the latter one is considered to be on convergence just below the H (1s) + $\bar{\mathrm{H}}$ (1s) dissociation threshold.

The structure of the resonance states is analyzed by a correlation function $C(r)$ and a radial distribution function $D(r)$ defined as

$$C(r') = \langle \Psi | \delta(\mathbf{r} - \mathbf{r}') | \Psi \rangle, \tag{57}$$

and

$$D(r') = r'^2 C(r'), \tag{58}$$

where Ψ is eigenfunction of $\bar{\mathrm{p}}$H/H$\bar{\mathrm{H}}$ close to the resonance state calculated by $\theta = 0$. $\langle \cdots \rangle$ means integration over all coordinates for a given $\mathbf{r}' = r'\hat{\mathbf{r}}$. Based on the correlation function between p and e^- of resonance states, the resonance states found in the present work are attributed to molecular(-ion) states. Besides, the present work finds that a characteristic correlation appears in radial distribution function at short range, which cannot be predicted by the Born-Oppenheimer approximation.

Not only the Coulomb force but also strong nuclear force act on the interaction between the proton and antiproton. The effects of the nuclear interaction on these resonance states are evaluated by introducing an optical potential operator for the p-$\bar{\mathrm{p}}$ interaction,

$$V_{\mathrm{p}\bar{\mathrm{p}}}(R) = V_{\mathrm{f.s.}}(R) + U_{\mathrm{nucl}}(R) + U_{\mathrm{ann}}(R), \tag{59}$$

where R is distance between the proton and antiproton, $V_{\mathrm{f.s.}}(R)$ is Coulomb potential modified by finite size of the proton/antiproton, $U_{\mathrm{nucl}}(R)$ is a real Woods-Saxon type potential describing strong force interaction, and $U_{\mathrm{ann}}(R)$ is an imaginary Woods-Saxon potential describing annihilation process. It has been known that the p-$\bar{\mathrm{p}}$ interaction results in a upper shift on Pn energy levels from the prediction by pure Coulomb interaction. The present work reveals that the upper shift caused by the p-$\bar{\mathrm{p}}$ interaction is suppressed by the leptons shielding the charges of proton/antiproton and the resonance states of $\bar{\mathrm{p}}$H/H$\bar{\mathrm{H}}$ predicted by the pure Coulomb interaction can remain below the dissociation threshold against the upper shift.

The finds of the present work are summarized in the following points:

- It is demonstrated that the non-adiabatic treatment for $\bar{\mathrm{p}}$H/H$\bar{\mathrm{H}}$ based on the Gaussian expansion method combined with the complex coordinate rotation method can predict the molecular(-ion)

resonance states located below $\bar{p}$ + H (1s) / H (1s) + $\bar{H}$ (1s) dissociation thresholds and can give resonance width (lifetime) against the spontaneous rearrangement dissociation.

- It is found that the radial distribution function between p and $\bar{p}$ of the molecular(-ion) resonance states shows a characteristic correlation in short range region. This characteristic correlation can be caused by spontaneous rearrangement between two canonical structures: $\bar{p}$ + H and Pn + e^- for $\bar{p}$H and H + $\bar{H}$ and Pn + Ps for H$\bar{H}$. In other words, it is shown that the spontaneous rearrangement is of importance to understand the static configuration of these molecular(-ion) resonance states as well as the resonance width (lifetime) against the spontaneous rearrangement dissociation. Schematic illustrations on these spontaneous rearrangement in the resonance structure are shown in Fig. 7.

- The stability of these resonance states are mainly characterized by the spontaneous rearrangement dissociation and the stability against the annihilation is smaller than the rearrangement dissociation. The resonance position is affected by the p-$\bar{p}$ interaction and shifts slightly on the shallower side.

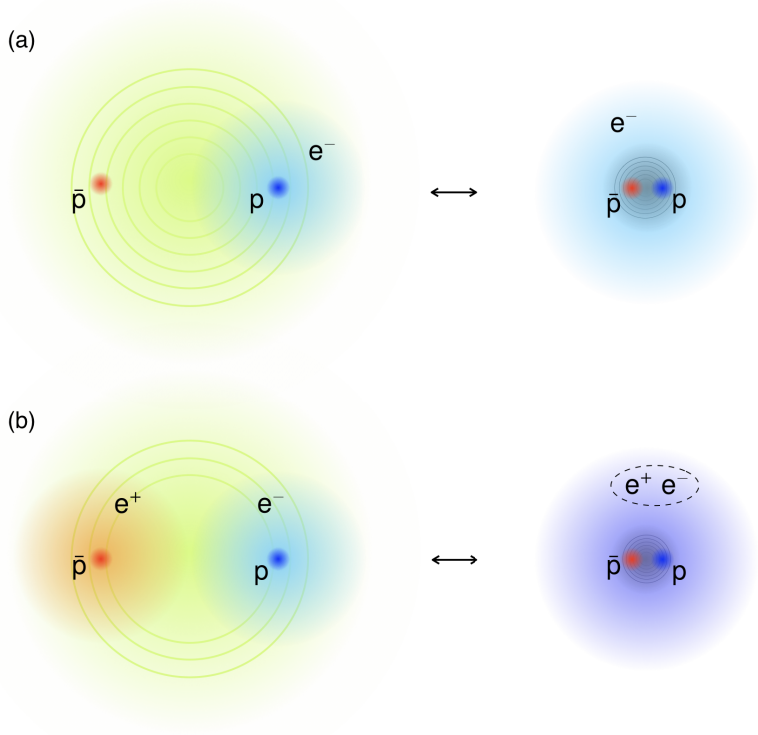

Figure 7: A schematic illustration of static structure of resonance states of $\bar{p}$H and H$\bar{H}$. (a) A situation where the resonance state of $\bar{p}$H shares a structure that the antiproton is associated with slightly polarized hydrogen atom mainly in s-wave and a structure where the electron is associated with a deformed protonium. (b) A situation where the resonance state of H$\bar{H}$ shares a structure that the antihydrogen atom is associated with slightly polarized hydrogen atom mainly in s-wave and a structure where the positronium is associated with a deformed protonium.

Chapter 5 Positronium anti-hydride molecule

An antihydrogen positive ion $\bar{H}^+ = \bar{p}e^+e^+$ is expected to be a new source of antimatter. $\bar{H}^+$ will be the first Coulombic system consisting of three antiparticles and it can be handled by electric field. The $\bar{H}^+$ can be utilized to produce an energy-tunable antihydrogen atom (ion) beam and to obtain an ultra-cold antihydrogen atom by sympathetic laser cooling with other positive ions, e.g. Be^+.

A reaction between an antihydrogen atom $\bar{H}$ and positronium atom (Ps) resulting in $\bar{H}^+ + e^-$ has attracted attentions for the upcoming experiment aiming to study the Gravitational Behavior of Antihydrogen at Rest (GBAR) [58, 59]. The reaction $\bar{H} + Ps \to \bar{H}^+ + e^-$ requires collision energy more than 6 eV, and it has other branches where the Ps is excited. Since the number of antihydrogen atoms prepared in experiments are limited for now and the lifetime of Ps is also short, theoretical searches of an effective reaction scheme of $\bar{H} + Ps \to \bar{H}^+ + e^-$ are indispensable to provide a sufficient number of $\bar{H}^+$ for future experiments. Since the reaction $\bar{H} + Ps$ is equivalent to a reaction of $H + Ps$, the difficulty of the theoretical calculation of this 4-body system comes from the positron's behavior involving a drastic rearrangement process during the scattering, $H + Ps \to H^- + e^+$.

The $\bar{H}$ and Ps has a single bound state at 1.065 eV below the lowest dissociation threshold $\bar{H}$ (1s) + Ps (1s). Positronium anti-hydride molecule $Ps\bar{H}$ is a charge-conjugated system of positronium hydride molecule (PsH) consisting of a proton, two electrons and a positron. The bound state can represent some aspect of the 4-body correlation in low-energy. Since the boundedness of the PsH was first shown by Ore [60], PsH has attracted attentions in quantum chemistry and atomic physics and has been studied both theoretically [61–70] and experimentally [71] as one of the simplest positronic molecules.

This chapter presents a study of a bound state of $Ps\bar{H}$ in section 5-1 and a study of scattering states including resonances in section 5-2. The scattering states in section 5-2 are calculated by using basis functions constructed in the similar way as described in the bound state calculation of section 5-1.

5-1 Bound state

Despite the achievement of highly accurate calculations on the binding energy of PsH, the structure and binding mechanism of this system has not been fully understood. The present work aims to analyze the structure of the PsH ($Ps\bar{H}$) with a Gaussian expansion method (GEM) [6]. The total wavefunction is constructed in terms of various rearrangement channel functions written in several coordinate systems corresponding to physical configurations. We examine the energy convergence depending on the channel functions included and analyze both of "molecular" and "atomic" pictures in bound state description. The "molecular" picture interprets the structure of PsH as a bound state of Ps and H while the "atomic" picture interprets the structure of PsH as a bound state of H^- and e^+. Looking ahead to the next scattering calculation, we use a notation of $Ps\bar{H}$ instead of PsH.

A part of the contents of this section is based on the following published work:

- Takuma Yamashita, Yasushi Kino, Emiko Hiyama, Svante Jonsell and Piotr Froelich, "A coupled rearrangement channel analysis of positronium antihydride", J. Phys.: Conf. Ser. **875**, 052031 (2017).

Method

The four-body Hamiltonian of positronium anti-hydride molecule except for the motion of the center-of-mass is given as

$$\hat{H}_{\mathrm{Ps\bar{H}}} = \sum_{i=1}^{4} -\frac{1}{2m_i}\nabla_{r_i}^2 + \frac{1}{2m_{\mathrm{G}}}\nabla_{r_{\mathrm{G}}}^2 - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} - \frac{1}{r_{24}} - \frac{1}{r_{34}}, \tag{60}$$

where m_i is a mass of particle i ($i = 1$: antiproton, $i = 2$: positron, $i = 3$: positron and $i = 4$: electron), m_{G} is a mass of the system, ∇_{r_i} is a differential operator for a position vector $\mathbf{r}_i$, $\nabla_{r_{\mathrm{G}}}$ is a differential operator for center of mass and r_{ij} is a relative distance between particles i and j.

We calculate a S-wave ground state wavefunction, Ψ_{JM} ($J = M = 0$), which satisfies the Schrödinger equation,

$$(\hat{H}_{\mathrm{Ps\bar{H}}} - E)\Psi_{00} = 0. \tag{61}$$

The wavefunction is expanded in terms of Gaussian functions and tripolar spherical harmonics $\mathcal{Y}^{(JM)}_{l_{ci}L_{ci}\lambda_{ci}}$ as

$$\Psi_{00} = \sum_c \sum_i (1 + \mathcal{P}) A_{ci} \mathcal{G}_{ci}^{l_{ci}L_{ci}\lambda_{ci}}(r_c,\, R_c,\, q_c) \mathcal{Y}^{(00)}_{l_{ci}L_{ci}\lambda_{ci}}(\hat{\mathbf{r}}_c,\, \hat{\mathbf{R}}_c,\, \hat{\mathbf{q}}_c), \tag{62}$$

where the radial part is written as $\mathcal{G}_{ci}^{l_{ci}L_{ci}\lambda_{ci}}(r_c,\, R_c,\, q_c) = r_c^{l_{ci}} R_c^{L_{ci}} q_c^{\lambda_{ci}} \exp(-a_{ci}r_c^2 - A_{ci}R_c^2 - \alpha_{ci}q_c^2)$, and $\mathcal{P}$ a permutation operator for two positrons. A coordinate system c is defined by a set of three different vectors ($\mathbf{r}_c$, $\mathbf{R}_c$, $\mathbf{q}_c$) to describe the four-body state. The linear coefficients A_{ci} of Eq. (62) and the eigenenergy E in Eq. (61) are determined by the Rayleigh-Ritz variational principle.

Results and discussion

The structure of $\mathrm{Ps\bar{H}}$ has been mainly investigated in three aspects. The first aspect is the "molecular" picture described in upper part of Fig. 8 (a) where Ps is associated with $\bar{\mathrm{H}}$. The second one is the "atomic" picture described in Fig. 8 (b) where $\bar{\mathrm{H}}^+$ is associated with e^-. The third one is a picture described in Fig. 8 (c) where Ps^+ is associated with $\bar{\mathrm{p}}$. The present work describes the molecular picture by introducing a coordinate system $c = 1$ shown in the lower part of Fig. 8 (a). Analogously, the atomic picture is described by the coordinate system $c = 2$ in the lower part of Fig. 8 (b) and the third picture is described by the coordinate system $c = 3$ in the lower part of Fig. 8 (c).

The present work investigates energy convergence of trial functions written in these coordinate systems. The inner angular momenta l_c, L_c and λ_c in Eq. (62) are truncated in finite value. It is found that the trial functions written in $c = 1$ shows faster convergence than other trial functions written in $c = 2$ and $c = 3$. Therefore, the major structure of $\mathrm{Ps\bar{H}}$ can be attributed to the molecular picture. As Frolov and Smith pointed out in Ref. [63], $\mathrm{Ps\bar{H}}$ could be described in the coexistent state of $\bar{\mathrm{H}}^+ + \mathrm{e}^-$ and $\bar{\mathrm{p}} + \mathrm{Ps}^+$. Certainly, the physical sum of three-body energy of $\bar{\mathrm{H}}^+$ and Ps^+ surprisingly shows a good agreement with the total 4-body energy of $\mathrm{Ps\bar{H}}$. On the other hand, the present calculation reveals that a trial function written in both of $c = 2$ and $c = 3$ gives slightly slower convergence than a trial function written in

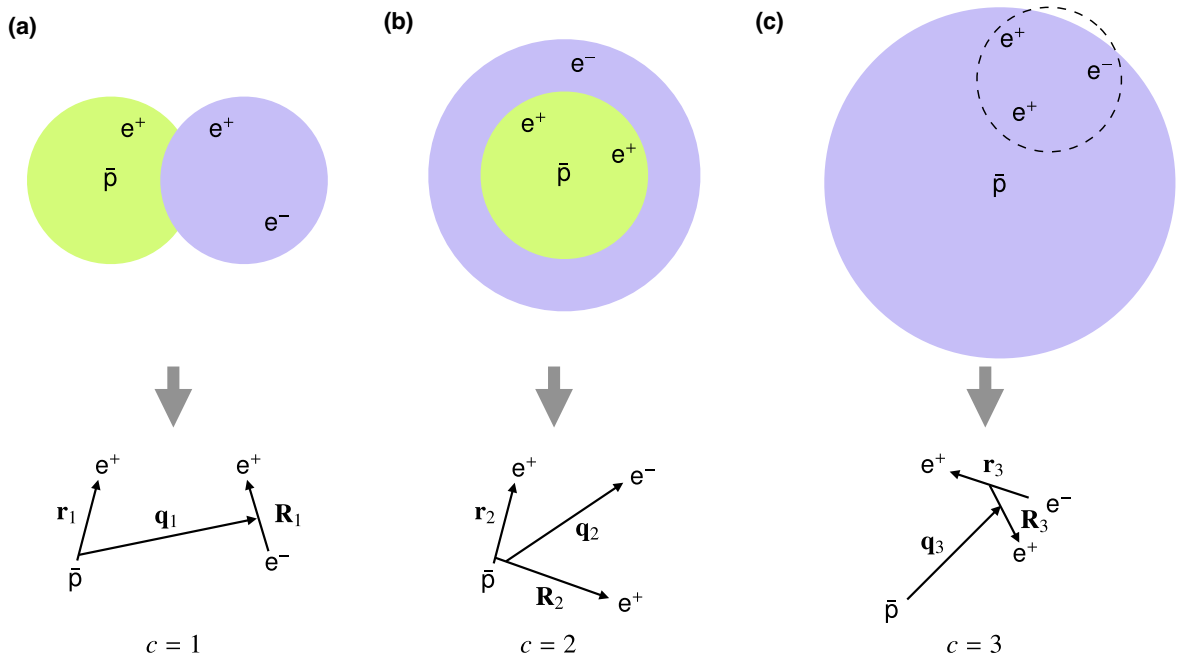

Figure 8: Schematic illustration for the structure of PsH̄: (a) a molecular picture where Ps is associated with H̄, (b) an atomic picture where $\bar{H}^+$ is associated with e^-, (c) a picture where Ps^+ is associated with $\bar{p}$. Coordinate systems shown in the lower part are used to describe the pictures in the upper part.

a single coordinate system $c = 1$. The present result suggests that the molecular picture is more usitable to understand the binding mechanism of PsH̄ than the double-structure picture.

The fact that the primary binding mechanism of PsH̄ is molecular picture apparently allows us to regard PsH̄ as a analogue of $\bar{H}_2$. It is also found that, however, the higher order inter-particle correlation in the molecular picture is different between in PsH̄ and in $\bar{H}_2$. The present work investigates the role of the tripolar spherical harmonics $\mathcal{Y}^{(00)}_{l_{ci}L_{ci}\lambda_{ci}}$ having non-zero inner angular momenta l_{ci}, L_{ci} and λ_{ci} by energy convergence. The analysis finds that in PsH̄, virtual excitation of both of Ps and H̄ from s-states to p-states contributes to the binding energy while the contribution of virtual excitation of H̄ accompanied by anisotropic relative motion between Ps and H̄. On the other hand, in $\bar{H}_2$, the virtual excitation of both of H̄'s from s-states to p-states shows smaller contribution to the binding energy than the virtual excitation of single H̄ accompanied by anisotropic relative motion between two H̄'s.

From a viewpoint of the second dominant correlation, namely the atomic picture, the present work investigates the positron-positron correlation in PsH̄ in connection with that in $\bar{H}^+$ where two positrons are not equivalent but they show different spatial distribution. A probability density map for a fixed e^+-$\bar{p}$-e^+ angle as a function of the distances of positrons from $\bar{p}$ is analyzed. It is found that the two positrons are squeezed by the electron but the repulsion between the two positrons overcomes the squeezing of the two positrons by electron. The probability density map supports an interpretation that the inequality between the two positrons becomes remarkable when they come in the same direction from $\bar{p}$.

By using the three coordinate systems shown in Fig. 8 as well as two auxiliary coordinate systems, the 4-body energy of Ps$\bar{\text{H}}$ is calculated precisely. The result reproduces the best variational result [70] by 0.000 003 hartree. Using this wavefunction, correlation functions and radial distribution functions between particles together with those between fragments (Ps and $\bar{\text{H}}$) are calculated. The correlation function is defined as

$$C(r_c') = \langle \Psi_0 \mid \delta(\mathbf{r}_c - \mathbf{r}_c') \mid \Psi_0 \rangle \,. \tag{63}$$

$C(r_c)$ provides information on the inter-particle probability distribution projected onto the coordinate $\mathbf{r}_c$. Since the ground state of Ps$\bar{\text{H}}$ is in S-symmetry, the $C(r_c)$ can be a good tool to investigate the structure. The radial distribution function is given by the correlation function as

$$D(r_c) = r_c^2 C(r_c). \tag{64}$$

These functions are compared with those of $\bar{\text{H}}_2$ and Ps_2. Ps$\bar{\text{H}}$ can be considered as an intermediary system between $\bar{\text{H}}_2$ and Ps_2 but unique features that are different from both of $\bar{\text{H}}_2$ and Ps_2 are found in the correlation/radial distribution functions.

5-2 Scattering states and resonances

In this section, a calculation of four-body scattering of $\bar{\text{H}}$ and Ps is presented. This reaction can be used to produce antihydrogen ion ($\bar{\text{H}}^+ \equiv \bar{\text{p}}\text{e}^+\text{e}^+$) which will open various sciences with manipulated antihydrogen atoms. For this aim, the present work develops a method to calculate both of elastic and inelastic scattering cross sections. In a slow collision of $\bar{\text{H}}$ (1s) and Ps (1s) where the collision energy is smaller than 0.1875 a.u., only the elastic scattering occurs. When the collision energy is larger than 0.1875 a.u., the Ps can be excited. In Fig. 9 (a), energies of dissociation thresholds are shown against the collision energy of $\bar{\text{H}}$ (1s) and Ps (1s). One can see that the second positronium excitation threshold, $\bar{\text{H}}$ (1s) and Ps ($n = 3$), is almost degenerated with $\bar{\text{H}}^+ + \text{e}^-$ dissociation threshold. Figure 9 (b) and (c) show the dissociation threshold energies measured from $\bar{\text{H}}$ (1s) + Ps ($n = 2$) threshold and $\bar{\text{H}}$ (1s) + Ps ($n = 3$) threshold, respectively. A slow collision between $\bar{\text{H}}$ (1s) and Ps ($n = 3$) is expected to produce the $\bar{\text{H}}^+$ with a large cross section. Supported by the recent development of manipulation technique of positronium [72], reactions between the excited positronium and an antihydrogen atom are becoming realistic.

The elastic scattering of the charge-conjugated system H (1s) + Ps (1s) has attracted attentions as one of the most fundamental scattering systems for the investigation of positronium-atom interaction [73–76]. A number of theoretical studies have revealed the H (1s) + Ps (1s) total/differential cross sections and scattering length [77–85]. One the other hand, the investigation of inelastic scattering has been limited to calculations of relatively high-energy collisions [86, 87] or calculations based on close-coupling method [88]. The present work develops a method that is adoptable to low-energy inelastic scattering of $\bar{\text{H}}$ (1s) + Ps (1s) and is capable of including all of the final dissociation states. By diagonalizing Hamiltonian in a finite space where 4-particles interact each other strongly with a help of GEM, we obtain an

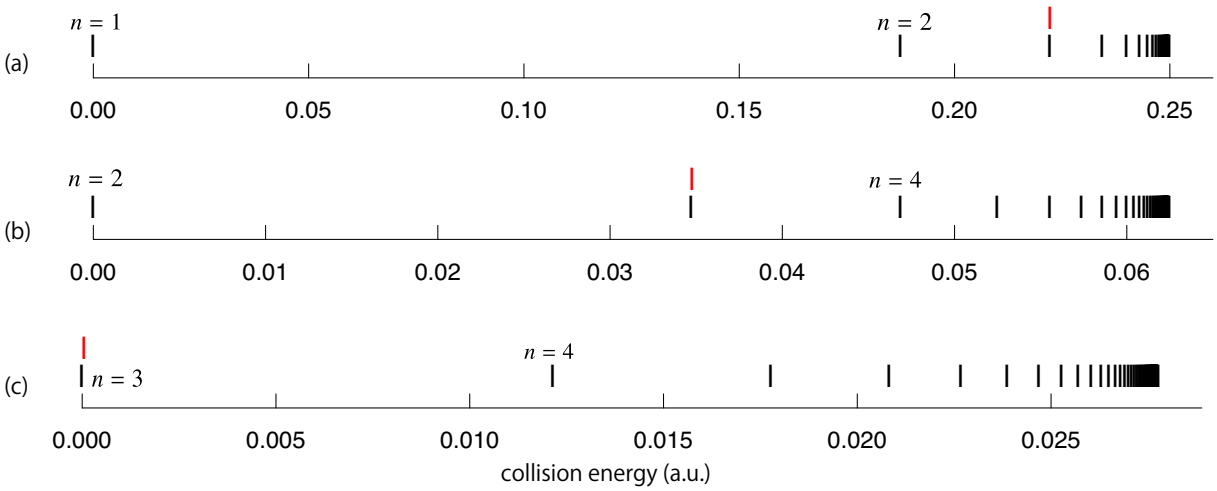

Figure 9: Dissociation energy levels of Ps$\bar{\text{H}}$ system. (a) Dissociation thresholds of $\bar{\text{H}}$ (1s) + Ps ($n \geq 1$) are shown in black line against collision energy of $\bar{\text{H}}$ (1s) + Ps (1s). The red line indicates dissociation threshold of $\bar{\text{H}}^+ + \text{e}^-$. (b) Dissociation thresholds of $\bar{\text{H}}$ (1s) + Ps ($n \geq 2$) are shown in black line against collision energy of $\bar{\text{H}}$ (1s) + Ps ($n = 2$). (c) Dissociation thresholds of $\bar{\text{H}}$ (1s) + Ps ($n \geq 3$) are shown in black line against collision energy of $\bar{\text{H}}$ (1s) + Ps ($n = 3$).

orthonormal basis set which are suitable to describe 4-body correlation and rearrangement during the collision. Under a proper boundary condition of scattering states, the total Hamiltonian for the full space is solved with the basis set.

Method

We first consider an elastic scattering state of $\bar{\text{H}}$ (1s) + Ps (1s). A total cross section σ can be expanded by the relative angular momentum λ of collision as

$$\sigma = \sum_{\lambda} \sigma^{(\lambda)}, \tag{65}$$

where $\sigma^{(\lambda)}_{cc_0}$ may be calculated by S-matrix element

$$\sigma^{(\lambda)} = \frac{\pi}{k^2}(2\lambda + 1)|1 - S^{(\lambda)}|^2. \tag{66}$$

Here, k is relative momentum between $\bar{\text{H}}$ (1s) and Ps (1s), $S^{(\lambda)}$ is S-matrix element. On the determination of $S^{(\lambda)}$, we use a wavefunction decomposed in terms of the total angular momentum J and its projection onto z-axis M,

$$\Psi^{(\lambda)} = \sum_{JM} \Psi^{(\lambda)}_{JM}, \tag{67}$$

where $\Psi^{(\lambda)}$ represents a wavefunction of the elastic channel $\bar{\mathrm{H}}$ (1s) + Ps (1s) having a relative angular momentum λ. In the case of the elastic scattering, since both of the fragments are s-state, the relative angular momentum λ is equal to the total angular momentum J.

In this work, a situation where the two positrons are spin-singlet is considered because the $\bar{\mathrm{H}}^+$ production occurs only from the spin-singlet scattering within non-relativistic framework. A wavefunction of elastic scattering of $\bar{\mathrm{H}}$ (1s) + Ps (1s) having total angular momentum $J = \lambda$ and its projection onto z-axis $M = m_\lambda$ can be written as

$$\Psi_{\lambda m_\lambda} = \frac{1}{\sqrt{2}}(1+\mathcal{P})\phi_{\bar{\mathrm{H}}(1\mathrm{s})}(r)\phi_{\mathrm{Ps}(1\mathrm{s})}(R)\frac{\chi_\lambda(\rho)}{\rho}\left[\left[Y_0(\hat{\mathbf{r}})\otimes Y_0(\hat{\mathbf{R}})\right]_0 \otimes Y_\lambda(\hat{\boldsymbol{\rho}})\right]_{\lambda m_\lambda} + \sum_\upsilon b_\upsilon \Phi_\upsilon^{(\lambda m_\lambda)}, \tag{68}$$

$\mathbf{r}$ is a vector sees a positron from antiproton, $\mathbf{R}$ sees another positron from electron, and $\boldsymbol{\rho}$ sees the center-of-mass of Ps from the center-of-mass of $\bar{\mathrm{H}}$. The first term in Eq. (68) expresses the asymptotic wavefunction. $\{\Phi_\upsilon^{(\lambda m_\lambda)}\}$ is a set of finite-range (square-integrable) functions calculated in a similar way as the bound state. The expansion with coefficients b_υ and functions $\Phi_\upsilon^{(\lambda m_\lambda)}$ facilitates the description of the four-body correlation of closed (non-asymptotic) part of the total wavefunction.

The scattering wavefunction in Eq. (68) can be extended to the situation where inelastic channels opens. The situation of the inelastic scattering is illustrated in Fig. 10. One has to include all asymptotic functions including both of initial and final states together with a proper description of 4 particles in the interaction region.

$$\Psi_{\lambda m_\lambda} = \sum_c \frac{1}{\sqrt{2}}(1+\mathcal{P})\phi_{\bar{\mathrm{H}}(1\mathrm{s})}(r)\phi_{\mathrm{Ps}}^{(c)}(R)\frac{\chi_{\Lambda_c}^{(c)}(\rho)}{\rho}\left[\left[Y_0(\hat{\mathbf{r}})\otimes Y_{L_c}(\hat{\mathbf{R}})\right]_{L_c} \otimes Y_{\Lambda_c}(\hat{\boldsymbol{\rho}})\right]_{\lambda m_\lambda} + \sum_\upsilon b_\upsilon \Phi_\upsilon^{(\lambda m_\lambda)}, \tag{69}$$

where L_c is an angular momentum quantum number of Ps in a final state c.

Results and discussion

Since the $\bar{\mathrm{H}}^+$ and e^- are attractive in asymptotic region, there is a series of resonances supported by the attractive Coulomb interaction between them. Above the first excitation threshold of positronium, the resonances have several dissociation branches. The present work reports partial cross sections from initial state $\bar{\mathrm{H}}$ (1s) + Ps (1s) to final states $\bar{\mathrm{H}}$ (1s) + Ps (1s) in s-wave (elastic scattering), $\bar{\mathrm{H}}$ (1s) + Ps (2s) in s-wave and $\bar{\mathrm{H}}$ (1s) + Ps (2p) in p-wave. It is found that cross section behavior of $\bar{\mathrm{H}}$ (1s) + Ps (1s) against the collision energy is strongly affected by the existence of the resonance states and there can be seen the Fano profile due to a large background phase shift. Two S-wave resonance states below the first excitation threshold of positronium and five resonance states above the threshold are found.

Resonance energies and partial widths are extracted from a fitting of the cross section by the Wigner's S-matrix formula. Unlike conventional resonance calculations with complex coordinate rotation method, the present calculation can distinguish each of final states. Therefore, partial widths of resonance states of Ps$\bar{\mathrm{H}}$ are calculated for the first time. It is found that these resonance states mainly decay into $\bar{\mathrm{H}}$ (1s) + Ps (1s) in s-wave, which is not a trivial feature because these resonance states above the first excitation

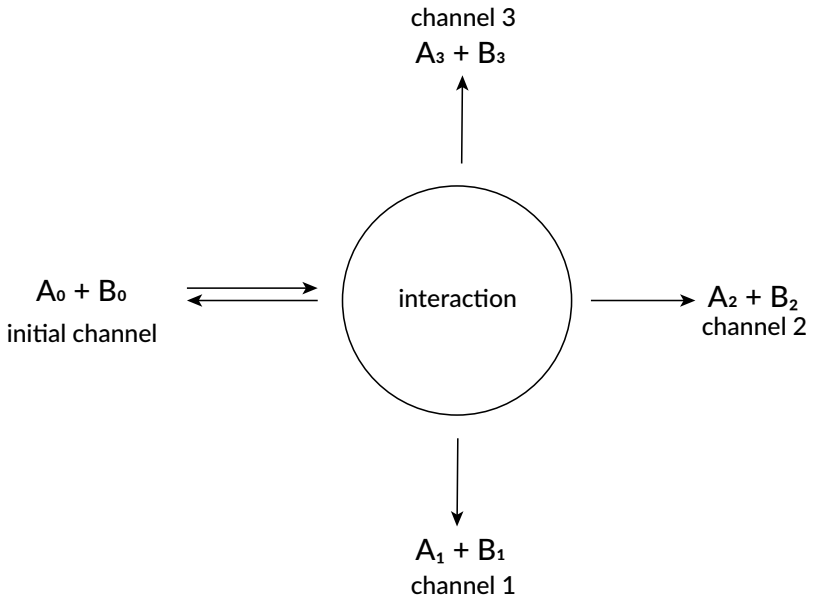

Figure 10: An illustration of inelastic channels. Two atoms A and B are in the initial states A_0 + B_0 and they collide each other. The A_0 + B_0 can result in different quantum states of A and B, A_c + B_c, via interaction during the collision. A channel c expresses a dissociation state of A_c + B_c.

threshold of positronium can decay into $\bar{H}$ (1s) + Ps (2s/2p) with much smaller energy transfer to the relative motion.

The inelastic resonance scattering calculation is further extended to prediction of production cross section of $\bar{H}$ (1s) + Ps (1s) $\rightarrow \bar{H}^+ + e^-$. It is found that the inelastic cross section of $\bar{H}$ (1s) + Ps (1s) $\rightarrow \bar{H}^+ + e^-$ begins from a finite value $\sim 1\ a_0^2$ above the threshold. When the relative motion of the dissociation fragments in the final state is slow and the inter-fragment interaction is the attractive Coulomb potential, the cross section near the threshold becomes constant [89]. Thus the present result is consistent with the threshold law derived by a detailed balance. The reaction $\bar{H}$ (1s) + Ps (1s) $\rightarrow \bar{H}^+ + e^-$ is the most dominant process among the inelastic process in the collision of $\bar{H}$ (1s) + Ps (1s). Blackwood *et al.* estimated the H^- production cross section from low energy scattering of H (1s) + Ps (1s) by close-coupling method and presented its cross section being $\sim \pi a_0^2$ [82]. The present work is consistent with the previous close-coupling calculation in the magnitude.

Chapter 6 Summary and Outlook

This thesis describes theoretical studies on an anti-hydride molecule and its sub/related systems with a perspective of "spontaneous rearrangement" driven by particle-antiparticle associations. Studies on three subjects are presented: (i) positronic atom, (ii) hydrogen anti-hydride molecule, and (iii) positronium anti-hydride molecule.

In the study (i), it is shown that in a loosely bound state of positronic alkali atom, relativistic corrections play a significant role. Based on an analysis of expectation values of relativistic correction operators, the enhancement of the role of relativistic corrections in binding energy is attributed to spontaneous rearrangement where the electron of positronium transfers to the nucleus. In the asymptotic region, the charge of the valence electron is screened by the positron, whereas near the nucleus, the electron is released from the positron and is subject to significant relativistic effects. Contrary to ordinary atomic/molecular systems where the relativistic effects are important in heavy elements, the relativistic effects on binding energy of positronic atoms can be enhanced by positron shielding the charge of electron even if the host atom is a light element, such as Li or Na. A positronic atoms having virtual positronium formation will be a suitable system for investigating relativistic and QED effects. While QED effects are also enhanced in heavy atoms, the perturbation expansion of the QED correction converges very slowly, depending on the nuclear charge. Systems which are sensitive to small relativistic/QED effects may be valuable to perform tests of fundamental physics.

The second focus in the study (i) is on the resonance states belonging to so-called dipole series which is originated to ion-dipole interaction between the excited positronium and the atomic ion. The present work investigates truncation of the series by channel coupling effects. The role of three-body correlation among the positron, a valence electron and an ion in these resonance states is examined. It is shown that the dipole resonance states correlate with atomic energy levels. While the relationship among resonance energies can be predicted analytically under simplification of the resonance structure, the spontaneous rearrangement between the positron-excited atom association and excited positronium-ion association results in truncation of the resonance series. These resonance series can be a platform for future experiments to synthesize positronic atoms by using laser-assisted radiative association.

In the study (ii), resonance states of hydrogen anti-hydride molecule and its subsystem, antiprotonic hydrogen atom, are investigated. Beyond conventional approaches based on adiabatic approximation, the present work demonstrates a non-adiabatic calculation of resonance states of the hydrogen anti-hydride molecule and antiprotonic hydrogen atom. Lifetime of these compounds, which cannot be extracted from the adiabatic calculations, as well as absolute resonance energies are presented. It is shown that spontaneous rearrangement plays an indispensable role in static structure of the resonance states as well as in stability or intramolecular reactivity against the automatic dissociation. Since the properties of hydrogen anti-hydride molecule are difficult to be predicted by the adiabatic approximation, it will become a good testing ground for a development of non-adiabatic theory. Besides, future works can utilize the present results of resonance states to predict synthesis of the hydrogen anti-hydride molecule and antiprotonic

hydrogen atom via radiative association. Moreover, the existence of the resonance states near threshold of H (1s) + $\bar{\mathrm{H}}$ (1s) / $\bar{\mathrm{p}}$ + H (1s) would affect the behavior of cross section in cold collision, which can be utilized as an indicator of purity and temperature of cold antihydrogen gas. It is also shown that the non-Coulombic interaction between proton-antiproton affects the positions of resonance states, which implies that these systems and related matter-antimatter compounds will be subjects both on chemistry and nuclear physics.

The study (iii) describes a detailed analysis of bound state of positronium anti-hydride molecule and an analysis to its resonance states based on scattering calculation. The present work demonstrates that the structure of the positronium anti-hydride molecule is supported by remarkable spontaneous rearrangement between an association of antihydrogen-positronium (molecular aspect) and another association of antihydrogen ion-electron (atomic aspect). It is shown that the molecular aspect of polarization mechanism of positronium anti-hydride molecule is different from that of hydrogen molecule. It is also demonstrated that in the atomic aspect positron-positron correlation resembles that in antihydrogen ion; however the molecular association disturbs the correlation.

Aiming at prediction of a reaction between antihydrogen atom and positronium to antihydrogen ion and electron, an *ab initio* calculation method which can deals with reaction cross sections between specific quantum states is developed. The scattering calculation reveals dissociation modes of resonance states between the antihydrogen ion and electron. A non-intuitive aspect of the dissociation via spontaneous rearrangement of positron, namely the dominant dissociation from the resonance states to H (1s) + $\bar{\mathrm{P}}$s (1s), is demonstrated. The present development can be adopted in near future to cold collision of antihydrogen atom and an excited positronium which can efficiently produce antihydrogen ion. The antihydrogen ion itself is intriguing as the first three-antiparticle system and it can be utilized to produce an energy-tunable antihydrogen beam which opens a variety of science based on matter-antimatter chemistry and an ultra-cold antihydrogen atom source which is suitable to test quantum gravity between matter and antimatter.

Understanding of antihydrogen-atom interaction will be a foundation to extend the study to molecular phase. Alhtough the investigations of antiatom-molecule interaction has been somewhat limited, positron-molecule interaction and antiproton-molecule interaction have been studied so far. The positron-molecule interaction has been attracted attentions in quantum chemistry [90–95] as well as in applications of positron to material science and medical treatment (positron emission tomography, PET) [96]. Dipole moment of polar molecule is related to the possibility that the molecule has a bound state with the positron [97]. One can see a similarity between the positronic molecule and the antiprotonic hydrogen atom (protonic antihydrogen atom) where the dipole moment between the proton and antiproton affects the electron (positron) behavior. An *ab initio* multi-component molecular orbital calculation and *ab initio* multi-component Monte Carlo calculation have predicted various positronic molecules [98, 99]. A vibrational Feshbach resonance (VFR) where the annihilation rate of positron on the molecule is enhanced by association with molecular vibration is a typical phenomena for positron-molecule interaction and has been studied both in calculations [100, 101] and experiments [102, 103]. In the antiproton-

molecule interaction, "chemical effect", e.g. factors of molecular structure or chemical environment, could affect the antiproton capture process. A negative muon (μ^-)-molecule system would resemble the antiproton-molecule system and the chemical effect on the capture process of the negative muon by the molecule has been studied experimentally [104, 105]. The $\bar{p}$-H_2 system is a fundamental system for antiproton-molecule systems and the reaction process involving protonium formation has been investigated theoretically [106–110]. The antiproton-molecule interaction is also of importance in future applications of antiproton beam to cancer therapy [111–114]. The antiatom-molecule interaction will involve more exotic and intriguing chemical phenomena.

The perspective of the spontaneous rearrangement in matter-antimatter compounds would play a role to bridge between matter-antimatter systems and matter systems. It is characteristic for the matter-antimatter system that the microscopic and drastic spontaneous rearrangement occurs. Since the spontaneous rearrangement is remarkable even in a small matter-antimatter system which can be analyzed by precise *ab initio* calculations, the knowledge on the rearrangement may provide a framework to investigate rearrangement in many-body matter systems. For example, a reaction between negative ion and positive ion has a similar aspect as a reaction between hydrogen and antihydrogen atom in a sense that nuclei are accelerated by the attractive potential. Correlation between the nuclear motion and leptonic motion in the hydrogen-antihydrogen reaction may provide an insight into such reaction embedded in plasma. It has been pointed out that $\bar{p}$ + H reaction has a similar aspect as H^- + H (1s) [115]. Spontaneous rearrangement seen in positronic atoms/molecules has a similar aspect as electron-hole interaction and perhaps atom-defect interaction in solid state. A large energy transfer to leptons by de-excitation of nucleus-antinucleus system in a matter-antimatter compound is similar to the Auger process in atomic systems and also to inter-atomic Coulombic decay in molecular systems. While the nature of matter-antimatter compounds might be exotic in some aspects, the nature comes from the same principle as matter. Only the difference of electric balance depending on charges and masses of constituents causes the exotic nature. The spontaneous rearrangement adopted in the present thesis is an attempt to open the potential correlations between chemistry in matter and that in matter-antimatter admixtures.

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